THE SYNTHESIS, STRUCTURE AND CHEMISTRY OF SUBSTITUENT-PERTURBED THIONE S-METHYLIDES AND S,S-DIHALOTHIONES

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

By

Anthony J. Arduengo, III

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in the School of Chemistry

Georgia Institute of Technology

August, 1976

THE SYNTHESIS, STRUCTURE AND CHEMISTRY OF

SUBSTITUENT-PERTURBED THIONE S-METHYLIDES

AND S,S-DIHALOTHIONES

Approved:

Edward M. Burgess, Chairman

Herbert O. House

Charles L. Liotta

Drury S. Caine

Date approved by Chairman: August 20, 1976

ACKNOWLEDGMENTS

The author is especially grateful to Dr. Edward M. Burgess for originating this project and for his helpful suggestions and guidance in every step of this work. For their reading of this thesis and their suggestions in its preparation, the author also wishes to thank Dr. Herbert O. House, Dr. Charles L. Liotta, and Dr. Drury S. Caine.

The author is indebted to the National Institutes of Health and the National Science Foundation for providing financial support of this work through grants.

Especially, the author is eternally grateful to his parents, family, and friends for their support, encouragement, and patience during the entire period of study.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF ILLUSTRATIONS

GLOSSARY OF ABBREVIATIONS

DABCO	1,4 diazabicyclo [2.2.2] octane
DMSO	dimethyl sulfoxide
HOMO	highest occupied molecular orbital
ir	infrared
LUMO	lowest unoccupied molecular orbital
nmr	nuclear magnetic resonance
TCNE	tetracyanoethylene
THF	tetrahydrofuran
TMS	tetramethylsilane

SUMMARY

The research described herein was to develop synthetic methods for the preparation of thiocarbonyl ylides and to investigate the electronic structure of substituent-perturbed thiocarbonyl ylides. In addition a new class of carbonium ion stabilized sulfuranes was synthesized and their structure and chemistry explored.

The deprotonation S-alkylthiouronium salts with appropriate electron withdrawing β-substituents provides the thiourea S-methylides. These 1,3-dipoles exhibited a variety of interesting reactions such as ylide ligand exchange, decomposition to alkenes, and ligand transfer from ylide to thione. A mechanism was offered for these reactions based on the formation of an intermediate hypervalent sulfur species.

Reaction of 1,3-dimethylimidazole-2-thione (4a) with α,α-bis(trifluoromethyl)-β,β-dicyanooxirane afforded 1,3-dimethylimidazole-2-thione S-dicyanomethylide (7a,x). Alkylation of 1,3-dimethylimidazole-2-thione with bromodiethylmalonate followed by dehydrohalogenation provided 1,3-dimethylimidazole-2-thione S-dicarboethoxymethylide (7a,z). The salt from the imidazolethione (4a) and methyl α-bromo-α-cyanoacetate was dehydrohalogenated to yield 1,3-dimethylimidazole-2-thione S-carbomethoxycyanomethylide (7a,y).

Ylides derived from tetramethylthiourea (4b) which were analogous to those in the imidazole series were also synthesized.

Attempts to isolate fluorenyl, anthronyl, and phenylcarboethoxy

ylides were unsuccessful, however, their decomposition products were identified.

SCF semiempirical calculations suggested that substituent perturbed thione methylides should have non-planar structures. An x-ray structure analysis of 1,3-dimethylimidazole-2-thione S-dicarboethoxymethylide (7a,z) supported this conclusion. NMR C^{13} and H^{1} shifts in the methylides versus some model compounds were correlated with the SCF bond orders and used to qualitatively describe the π-conjugation between charged centers in these 1,3-dipoles.

MINDO/3 calculations on a model system (thiourea S-diformylmethylide) revealed low barriers to rotation of both carbon termini and a preferred non-planar structure different from the planar "allyl anion" structure. The conrotatory motion of the termini out of the allyl anion form was preferred over the corresponding disrotatory motion. The x-ray structure of 7a,z showed a carbonium ion and carbanion center orbital orientations of 33.9° and 14.5° respectively with reference to the CSC plane. The orbital orientations were also found to be conrotatory. Proton nmr's on a series of imidazole ylides suggested the presence of charge transfer across the CSC ylide system.

Carbon-13 nmr shifts of the thiourea thiocarbonyl carbon showed a strong paramagnetic contribution. The shifts of this carbon over a series of compounds (tetramethylthiourea, tetramethylthiourea S-methyl iodide and the tetramethylthiourea S-dicarboethoxymethylide) were correlated to the parameters from a CNDO/2 calculation. Assumptions were made of a small constant diamagnetic contribution, a major contribution from the Z component of the paramagnetic shielding tensor and

that the ΔE term in the Pople-Karplus equation could be approximated by the local $n_s \rightarrow \pi^*$ transition. The correlation with the Pople-Karplus equation was extremely good and revealed a relation between a Mulliken overlap population and the C^{13} chemical shift.

The action of one-half equivalent of bromine on 1,3-dimethylimidazole-2-thione (4a) provided excellent yields of bis(1,3-dimethylimidazolium)disulfide dibromide (34). Treatment of 34 with a second half equivalent of bromine resulted in the formation of the hypervalent S-dibromide (31). Calculations on a model system showed that the energy surface for rotation about the CS bond contained two minima. The planar structure (30) was favored by 2.0 ev over the perpendicular structure (29) on an electronic basis, however, if steric factors were considered in addition to the electronic factors the perpendicular structure (29) was the most stable.

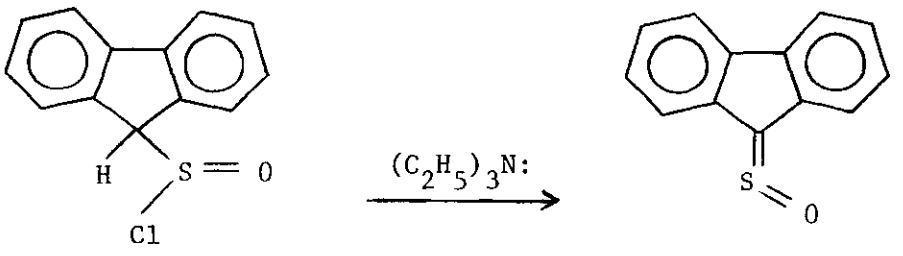
Extended Huckel calculations revealed that while the dibromosulfurane (31) should be covalent, the cyano-bromo sulfurane (33) should be ionic with a separated bromide ion. X-ray structure analysis of the dibromosulfurane (31) and the cyano-bromo sulfurane (33) were in accord with the structures based on Extended Huckel calculations.

CHAPTER I

INTRODUCTION

Thione S-methylides, thione S-imides, and sulfines have been of great interest to both the experimental and theoretical chemist for several years. To date representative members of all three classes of compounds have been synthesized and studied.

Sulfines have been prepared by the dehydrohalogenation of a precursor sulfinyl chloride such as 1,[1,2] the oxidation of monomeric thioketones[3,4] and the thioketene 2,[5] and more recently by the base hydrolysis of α-chlorosulfenyl chlorides.[6]



1

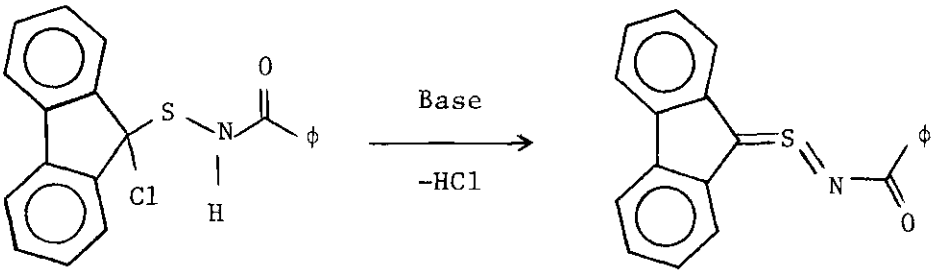
$$[(CH_3)_2C]_3C{=}C{=}S \quad \overset{[O]}{\rightarrow} \quad [(CH_3)_3C]_2C{=}C{=}S{=}O$$

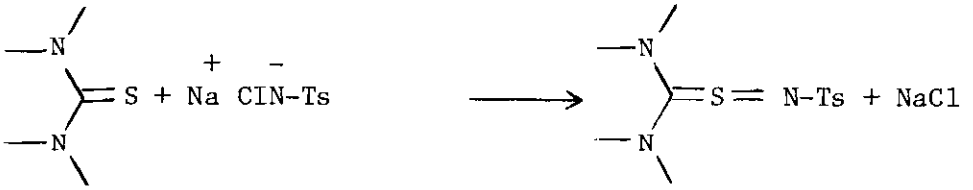
2

Sulfines generally show fair stability and are easily isolated.

Thione S-imides have been synthesized by the action of base on α-chloromethanesulfenamides[7] and be the condensation of Chloramine-T

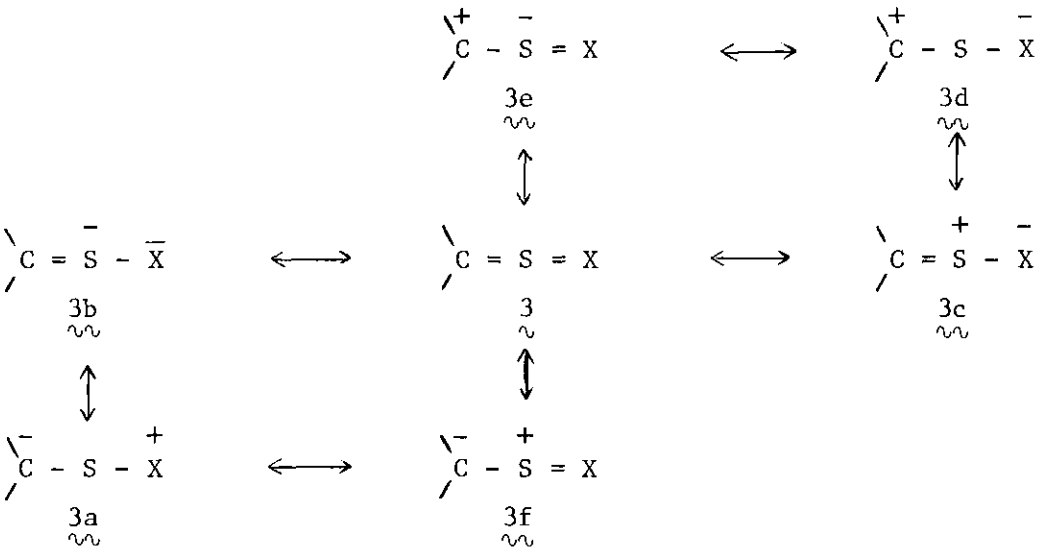
with thioureas.[8]





Thiones S-imides show varied stability allowing the isolation of many representative compounds.

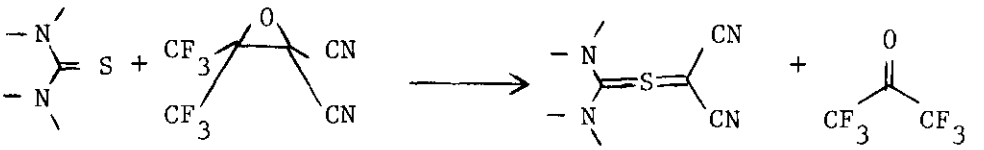
The stability of both sulfines and thione S-imides can be attributed to the resonance contributors of structure 3.



X = O,N-R or $C(R)_2$

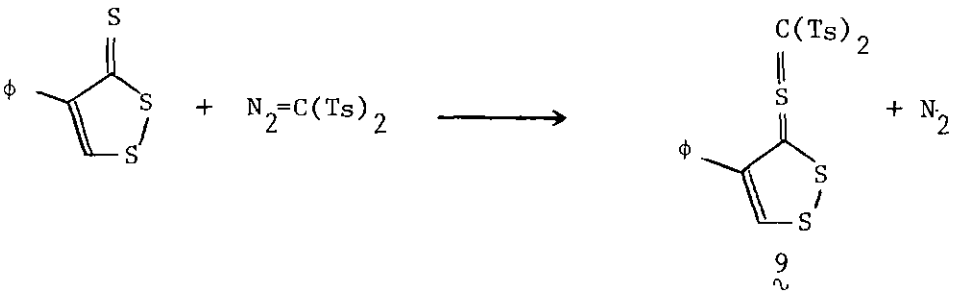
The most stable sulfines and thione S-imides can be expected to have major contributions from resonance structures 3c and 3d since both oxygen and nitrogen should best sustain high electron density.

Thione S-methylides have been synthesized successfully by a number of routes. W. J. Middleton reported in 1966 that 1,1,3,3-tetramethyl-2-thiourea S-dicyanomethylide (7b,x) could be synthesized by the action of α,α-bis(trifluoromethyl)-β,β-dicyanooxirane on tetramethylthiourea (4b).[10]



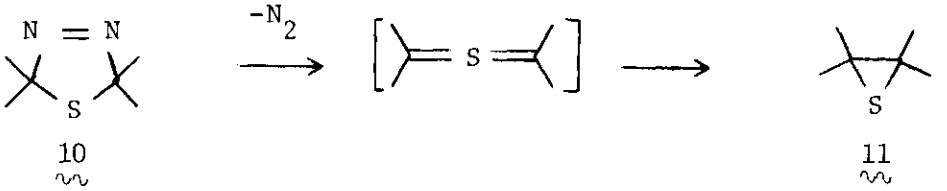
4b 7b,x

In 1972 Oae reported the synthesis of the thione S-methylide, 9, from the decomposition of ditosyldiazomethane in the presence of a nucleophilic thione.[11]



9

R. M. Kellogg in 1972 reported on a detailed study of thione S-methylides which were formed by the loss of nitrogen from a dihydrothiadiazole, 10.



10 11

Kellogg was also able to show that ylides which were not substituent perturbed underwent the Woodward-Hoffmann[13] allowed conrotatory closure to the thiirane, 11. Kellogg's successful application of an "allyl anion" bonding model to the observed pericyclic chemistry of 1,3 dipolar ylides has led to much theoretical interest in the pericyclic chemistry of these and related systems.[14,15]

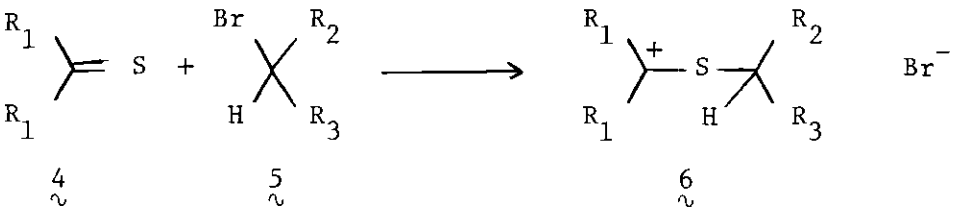
The potential surface for conrotation of a thione S-methylide to a thiirane is to the first approximation dependent upon the energetic behavior of key high-lying molecular orbitals as determined by the conservation of orbital symmetry.[14] Snyder has calculated the shape of the one dimensional surface for the conversion of an unperturbed symmetric planar thione S-methylide to the corresponding thiirane, using a conrotatory motion (the forbidden disrotatory transition state lies > 7 Kcals/mole above the allowed one) in agreement with the stereochemistry observed by Kellogg.[10,14,15] The alteration of this surface by a

large deviation from symmetry could possibly provide intermediates of lower energy than either end-point reactant as well as change the preference for a particular ring closure mode as indicated by a recent theoretical investigation.[15] Thus, the synthesis of substituent-perturbed thione S-methylides should provide molecules whose ring closure energetics are quite different from the unperturbed systems.

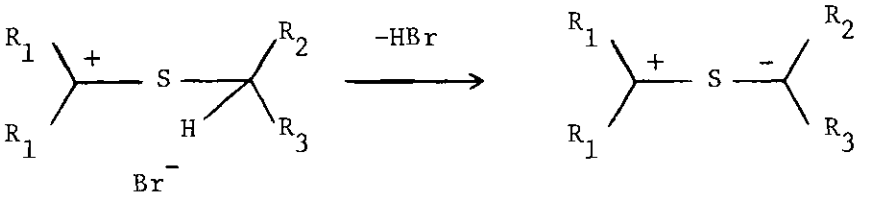
In terms of resonance stability, the perturbed thione S-methylides should have large contributions from structures 3c and 3d and could possibly be more stable than an unperturbed system.

The best combination of substituents would be one in which one carbon was substituted with electron donating groups to stabilize a carbonium ion while the second carbon was substituted with electron withdrawing functions for carbanion stabilization. This substitution pattern also suggests that thiouronium S-methyl salts might serve as intermediates in synthesis.

Alkylation of a thiourea or other electron rich thione (4) with a reagent which is substituted with good electron withdrawing functions should yield a salt, 6, whose base catalysed deprontonation would provide the S-methylide, 7.

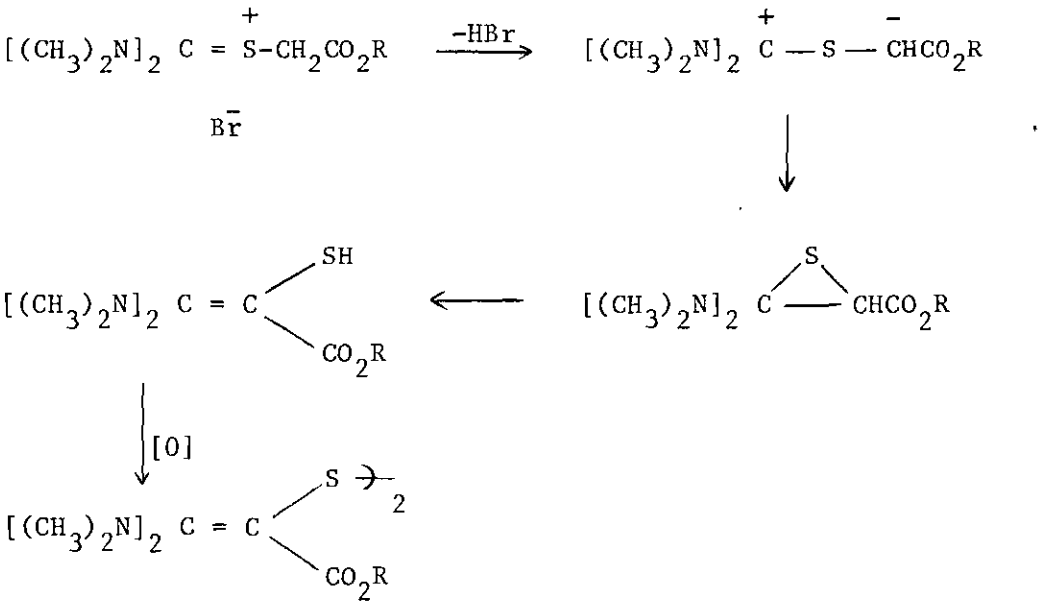


4 5 6



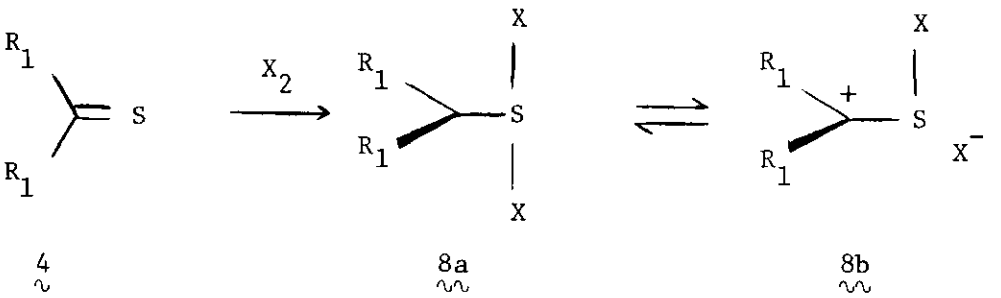
6 7

This approach to synthesis was attempted by Nozaki and co-workers who reported in 1969 that only products from decomposition of the thione S-methylide could be isolated.



Nozaki's work, while actually unsuccessful in isolating thione S-methylides, does provide the only example of a decomposition route for the perturbed thione S-methylides. Stronger perturbations could lead to yet another decomposition mode.

Another possible synthetic route to the thione S-methylides would involve the intermediary of an S,S-dihalothione (8a-b). These compounds, which are as yet unknown, could possibly be synthesized by the action of a halogen on a thione, 4.



4 8a 8b

These dihalothiones could be hypervalent systems existing mostly as the valence tautomer 8a. This structure contains the feature of a three center electron-rich bond stabilized by an adjacent carbonium ion. The hypervalent system, X-S-X, is most closely related to the tetracoordinate tetracovalent sulfurances studied by Martin and coworkers.[16,17]

The chemical literature is replete with articles expressing great theoretical interest in hypervalent molecules and many models have been developed which represent electron-rich orbital deficient bonding.[18-23]

Only in one instance has the role of equatorial substituents been investigated for their influence on the hypervalent system.[21]

Hoffmann, Howell, and Mutterties[21] have investigated the parent phosphorane, PH_5, and discussed possible influences of equatorial π-systems on the hypervalent bond. For a structure such as 12 these workers concluded that the orientation of an equatorial π-system will vary depending upon the occupancy of the equatorial p-orbiatl.

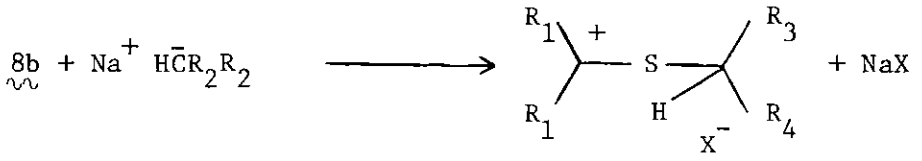
12a 12b

Structure 12a should be preferred if the equatorial p-orbital were electron deficient (as would be the case for the dihalothiones which should have an equatorial carbonium ion). Structure 12b would be preferred if the equatorial p-orbital were electron rich (e.g., a lone pair). Interestingly, though, Hoffmann and co-workers predicted that "π-acceptors will prefer axial sites, π-donors equatorial positions," so that the orientation of π-acceptors in the equatorial plane has little meaning.

Although the dihalothiones would be a different case from the phosphoranes because of the presence of lone pairs on sulfur some of the fundamental conclusions about hypervalent bonding systems should, nonetheless, be valid.

The adjacency of a carbonium ion might provide sufficient stabilization of the hypervalent system that more unstable bonding systems could be explored. One extreme case would be a sulfurane with axial iodines.

Because the dihalothiones would be closely related to the tetracovalent sulfuranes studied by Martin and co-workers[16,17] the same type of chemistry might be observed. For example, Martin has shown that the tetracovalent sulfuranes will undergo ligand exchanges to give new sulfuranes. If this same reaction were to occur for the dihalothiones it would allow the formation of thiouronium salts, 6, from carbon bases.



As before these thiouronium salts could be deprotonated to give thione S-methylides.

Thus it is the goal of the research described herein to synthesize highly perturbed thione S-methylides via thiouronium salts and explore their structure and chemistry. And furthermore, attempts will be made to synthesize dihalothiones (sulfuranes) and investigate their structure

and usefulness as synthetic intermediates.

CHAPTER II

INSTRUMENTATION AND EQUIPMENT

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Hexane, pentane, and benzene were washed with concentrated sulfuric acid and then distilled from sodium metal. Triethylamine, acetonitrile and methylene chloride were distilled from powdered phosphorous pentoxide. Methanol and ethanol were distilled from calcium hydride. Ether, anhydrous and USP, was purchased commercially in one pound cans and used without further purification. Purification of all other organic reagents was achieved by established procedures.[46] Inorganic chemicals were commercially available reagent grade.

Anhydrous reaction conditions were established by drying the necessary glassware in an oven maintained at 150°C. An inert atmosphere was provided by purified argon which had been dried by passing through a coiled glass tube immersed in a dry ice-acetone bath. In all reactions where triethylamine hydrochloride or 1,4 diazabicyclooctane (DABCO) hydrochloride were produced, their identity was confirmed by melting point and comparison of the infrared spectra with that of an authentic sample. In cases where the possibility existed that more than one product might be formed in a reaction, the crude reaction mixture was subjected to nmr and ir analysis, and, unless otherwise indicated, only the products isolated and characterized were observed in the crude mixture.

Concentration or evaporation of solvents was done under reduced

pressure (ca 20 mm Hg) with the aid of a Buchi Rotavapor rotary evaporator. Thin layer chromatography was performed using Eastman Chromagram sheets.

Osmotic molecular weights were determined on a Mechrolab vapor pressure osmometer (model 301A) at 37°C and in each case the solvent is specified. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-7L high resolution mass spectrometer with an 80 electron volt source. Proton nuclear magnetic resonance spectra (nmr) were recorded on a Varian Associates model T-60A spectrometer in the solvent specified in each case. Chemical shifts were reported versus an internal tetramethylsilane (TMS) standard and the abbreviations s, d, t, q, and m refer to singlet, doublet, triplet, quartet, and multiplet, respectively. Carbon-13 nuclear magnetic resonance spectra were obtained on a Jeol model PFT-100 Fourier transform nmr spectrometer and the chemical shifts are reported versus a tetramethylsilane standard in the same manner as proton nmr. Infrared spectra were obtained on a Perkin-Elmer model 457 recording spectrophotometer using either 0.1 mm sodium chloride cells or a potassium bromide wafer. Ultraviolet spectra were recorded on a Beckman DB-GT spectrophotometer using one centimeter balanced quartz cells. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are not corrected. Melting points are reported in degrees centigrade.

Data for x-ray structure analysis was collected on a Syntex $P2_1$ four circle diffractometer equipped with a graphite monochromator using MoK_α radiation at a takeoff angle of 6.5°. Unit cell parameters and the

orientation matrix were determined by the diffractometer from fifteen reflections of varied 2θ values. For the solution and refinement of structure, computations were performed using standard programs[47] and were carried out on the Control Data Cyber 74 system and in all cases the final R factor is reported along with the unit cell and space group information.

Molecular orbiatl calculations were performed using either Extended Huckel, CNDO-INDO or MINDO/3 programs and the computations were carried out on a Control Data Cyber 74 system.

Elemental analyses (C, H, N, S, and halogen) were performed by Atlantic Microlab, Inc., Atlanta, Georgia.

CHAPTER III

EXPERIMENTAL

1,3-Dimethylimidazolium Iodide

Methyl iodide (143.0 g, 1.0 mole) in 75 ml anhydrous methylene chloride was added dropwise over a period of 30 minutes to 82.11 g (1.0 mole) of 1-methylimidazole in 200 ml methylene chloride maintained at 5° C. When the addition was complete the cooling bath was removed and the reaction mixture was allowed to stir for an additional 30 minutes at room temperature. The methylene chloride was removed by a rotary evaporator to yield 224.0 g (100%) of the 1,3-dimethylimidazolium iodide: mp 82-83°C; Proton nmr (DMSO-d_6) δ 9.86 (s,1H), δ 7.75 (s,2H), and δ 4.08 (s,6H); Carbon-13 nmr (DMSO-d_6) δ 136.69 (s), δ 123.04 (s), δ 36.10 (s).

Anal. Calculated for $C_5H_9N_2I$: C, 26.78; H, 4.02; N, 12.50. Found: C, 26.56; H, 4.13; N, 12.40.

1,3-Dimethylimidazole-2-Thione (4a)

1,3-Dimethylimidazolium iodide (44.8 g, 0.20 mole), Lac sulfur (20.0 g, 0.625 mole), and anhydrous potassium carbonate (30.0 g, 0.22 mole) were suspended in 400 ml anhydrous methanol. The mixture was stirred at 27° for 24 hours, filtered, and the filtrate was reduced to one-third volume with a rotary evaporator. On cooling to -30° the mother liquor deposited crystals of the thione which were separated by filtration. The solid which was collected in the initial filtration was

extracted with 250 ml boiling water. The water extract was cooled to 10° and deposited additional thione. All of the crude thione was combined and recrystallized from water to yield 22.7 g (88%) of the imidazolethione as coloreless needles: mp 181-183°; Proton nmr ($CDCl_3$) δ 6.68 (s,2H), δ 3.6 (s,6H); Carbon 13 nmr (DMSO-d_6) δ 161.87 (s), δ 117.82 (s), δ 34.34 (s); Osmotic molecular weight ($CHCl_3$) 128.0; ir ($CHCl_3$) 2940 (C-H), 1450 and 1380 cm^{-1}.

Anal. Calculated for $C_5H_8N_2S$: C, 46.88; H, 6.25; N, 21.88; S, 25.00. Found: C, 46.81; H, 6.31; N, 21.80; S, 25.02.

Reaction Of 1,1,3,3-Tetramethyl-2-Thiourea With Bromoalononitrile

1,1,3,3-Tetramethyl-2-thiourea (2.64 g, 0.02 mole) in 40 ml anhydrous methylene chloride was added dropwise over a period of 20 minutes to 2.9 g (0.02 mole) of bromomalononitrile in 100 ml methylene chloride maintained at 0°. When the addition was complete the solution was stirred at 0° for an additional 15 minutes. The solvent was removed on a rotary evaporator to yield a brown intractable mass from which 1.7 g (65 percent) 1,1,3,3-tetramethyl-2-thiourea could be extracted with diethyl ether. There was no evidence for the formation of the desired ylide hydrobromide.

Reaction Of 1,3-Dimethylimidazole-2-Thione With Bromonalononitrile

1,3-Dimethylimidazole-2-thione (2.56 g, 0.02 mole) in 75 ml anhydrous methylene chloride was added dropwise over a period of 30 minutes

to 2.9 g (0.02 mole) of bromomalononitrile in 100 ml methylene chloride maintained at 0°. When the addition was complete the reaction was stirred for an additional 30 minutes at 0°. The methylene chloride was removed to yield a brown-black solid from which 1.7 g (47 percent) 1,3-dimethylimidazole-2-thione was extracted with hot water. There was no evidence for the formation of the desired ylide hydrobromide.

1,1,3,3-Tetramethyl-2-Thiourea S-Dicyanomethylide (7b,x)

1,1,3,3-Tetramethyl-2-thiourea S-dicyanomethylide was prepared from tetramethylthiourea and α,α-bistrifluoromethyl-β,β-dicyanooxirane according to the procedure of W. J. Middleton.[10] The produce was isolated as colorless needles: mp 70-72° (dec.), (lit.[10] 70°): Osmotic molecular weight ($CHCl_3$) 194.0.

1,3-Dimethylimidazole-2-Thione S-Dicyanomethylide (7a,x)

1,3-Dimethylimidazole-2-thione (6.4 g, 0.05 mole) in 75 ml anhydrous methanol was stirred at 0° while 11.5 g (0.05 mole) of α,α-bistrifluormethyl-β,β-dicyanooxirane was added in 1 g portions. The yellow solution was cooled to -30° and deposited light yellow crystals of the ylide. The crude product was recrystallized from methanol of give 3.5 g (99%) of 7a,x: mp 96° (dec.); ir ($CHCl_3$) 2110 and 2150 cm^{-1} (C≡N); Proton nmr (DMSO-d_6) δ 3.80 (s,3H), and δ 7.82 (s,1H); Carbon-13 nmr (DMSO-d_6) δ 144.16 (s), 124.80 (s), 123.52 (s), 39.44 (s), 9.89 (s); Osmotic molecular weight ($CHCl_3$) 193.0.

Anal. Calculated for $C_8H_8N_4S$: C, 50.00; H, 4.17; N, 29.17; S, 16.67. Found: C, 49.97; H, 4.15; N, 29.22; S, 16.62.

All of the isolated thione S-methylides reported in this work were stable at room temperature for several hours. The ylides could be stored at -30° for up to three months and indefinitely if the temperature was kept about -78°.

1,3-Dimethylimidazole-2-Thione S-Dicarboethoxymethylide Hydrobromide (6a,z)

1,3-Dimethylimidazole-2-thione (12.8 g, 0.1 mole) in 100 ml anhydrous methylene chloride was added dropwise to a solution of 23.9 g (0.1 mole) of diethyl bromomalonate in 100 ml methylene chloride. The solution was stirred for 3 hours at 27° and then reduced to 100 ml on a rotary evaporator. The mixture from which solid had begun to separate was diluted with 100 ml anhydrous diethyl ether. The mixture was then cooled to -30° and allowed to stand for 12 hours. The solid formed was collected by filtration and recrystallized from chloroform-ether to give 23.6 g (90%) of the ylide hydrobromide: mp 150-153° (dec.); ir ($CHCl_3$) 1720 (C=O) and 2910 cm^{-1} (C-H); Proton nmr ($CDCl_3$) δ 1.22 (t,6H), δ 4.15 (s,6H), δ 4.23 (q,4H), δ 5.05 (s,1H), δ 8.3 (s,2H).

Anal. Calculated for $C_{12}H_{19}BrN_2O_4S$: C, 39.23; H, 5.18; N, 7.63; S, 8.72. Found: C, 39.07; H, 5.23; N, 7.72; S, 8.80.

1,3-Dimethylimidazole-2-Thione S-Dicarboethoxymethylide (7a,z)

Triethylamine (1.01 g, 0.01 mole) was added dropwise over 10 minutes to 6a,z (3.67 g, 0.01 mole) in 50 ml anhydrous methanol maintained at 0°. When the addition was complete the solution was cooled

to -30° and allowed to stand for 2 hours. The reaction mixture was then filtered to collect the crystalline ylide with a slight amount of triethylamine hydrobromide as an impurity. The crude solid was recrystallized from methanol to yield 2.5 g (87%) of the ylide as colorless crystalline plates: mp 170-171° (dec.); ir ($CHCl_3$) 1650 (C=O), 1755 (imidazolium) and 3070 cm^{-1}(C-H); Proton nmr ($CDCl_3$) 7.0 (s,1H), 4.10 (q,2H), δ 3.97 (s,3H), δ 1.23 (t,3H); Carbon-13 nmr (DMSO-d_6) δ 168.0 (s), δ 146.30 (s), δ 122.34 (s), δ 59.06 (s), δ 58.13 (s), δ 35.00 (s), δ 15.02 (s). Osmotic molecular weight ($CHCl_3$) 288.0.

Anal. Calculated for $C_{12}H_{18}N_2O_4S$: C, 50.35; H, 6.29; N, 9.79; S, 11.19. Found: C, 50.43; H, 6.30; N, 9.85; S, 11.09.

1,1,3,3-Tetramethyl-2-Thiourea S-Dicarboethoxymethylide Hydrobromide (6b,z)

1,1,3,3-Tetramethyl-2-thiourea (13.2 g, 0.1 mole) in 60 ml anhydrous methylene chloride was added dropwise over a period of 15 minutes to 23.9 g (0.1 mole) diethyl bromomalonate in 100 ml methylene chloride at 27°. The reaction mixture was then stirred an additional 6 hours at this temperature after the addition was complete. The methylene chloride was removed on a rotary evaporator to leave an oily residue. The oil was dissolved in chloroform-ether and cooled to -30°. Only oil separated upon cooling and after repeated diethyl ether extractions the oily salt was dried in vacuo and used without further purification. The yield was 37.0 g (100%): ir ($CHCl_3$) 2930 (C-H), 1732 (C=O), 1610 cm^{-1}; Proton nmr ($CDCl_3$) δ 5.0 (s,1H), δ 4.33 (q,4H), δ 3.58 (s,12H); δ 1.45 (t,6H).

Anal. Calculated for $C_{12}H_{23}N_2O_4SBr$: C, 38.78; H, 6.19; N, 7.54; S, 8.62; Br, 21.55. Found: C, 38.69; H, 6.12; N, 7.50; S, 8.56; Br, 21.66.

1,1,3,3-Tetramethyl-2-Thiourea S-Dicarboethoxymethylide (7b,z)

Triethylamine (1.01 g, 0.01 mole) was added dropwise over a 10 minute period to a soluiton to 6b,z (3.71 g, 0.01 mole) in 75 ml anhydrous methylene chloride maintained at 0°. The solution was stirred for 15 minutes at 0° after the addition was complete. The volume was reduced to 75 ml on a rotary evaporator. Diethyl ether was added precipitate the triethylamine hydrobromide and the mixture was filtered. The filtrate was evaporated to yield an oil which was crystallized after extraction of impurities with ether-pentane. The crude product was recrystallized from ether methanol to give 1.7 g (58%) of the ylide as colorless plates: mp 104-106° (dec.); ir ($CHCl_3$) 2994 (C-H), 1645 (C=O), and 1580 cm^{-1} (iminium); Proton nmr ($CDCl_3$) δ 4.12 (q,2H), δ 3.2 (s,6H), δ 1.23 (t,3H); Carbon-13 nmr (DMSO-d_6) δ 180.80 (s); δ 165.75 (s), δ 59.76 (s), δ 56.79 (s), δ 42.17 (s), δ 14.92 (s); Osmotic molecular weight ($CHCl_3$) 294.0.

Anal. Calculated for $C_{12}H_{22}N_2O_4S$: C, 49.70; H, 7.58; N, 9.66; S, 11.02. Found: C, 49.52; H, 7.49; N, 9.60; S, 10.98.

Methyl α-Bromo-2-Cyanoacetate

Bromine (80.0 g, 0.5 mole) and potassium hydroxide (28.0 g, 0.5 mole) in 300 ml distilled water and added dropwise over a 3 hour period

to a stirred solution of 49.5 g methyl cyanoacetate in 800 ml distilled water and 75 ml methylene chloride maintained at 5°. After the addition was complete the methylene chloride layer was separated from the aqueous layer. The aqueous layer was extracted twice with 50 ml portions of methylene chloride. The methylene chloride solutions were combined and dried over anhydrous magnesium sulfate. The methylene chloride was removed and the oily product was distilled at 65-70° (2.5 mm Hg)(lit.[25] bp 90-92° (9.0 mm Hg). Proton nmr ($CDCl_3$) 5.08 (s,1H), 3.92 (s,3H).

1,3-Dimethylimidazole-2-Thione S-Carbomethoxycyanomethylide Hydrobromide (6a,y)

1,3-Dimethylimidazole-2-thione (2.56 g, 0.02 mole) in 70 ml dry THF was added dropwise to 3.56 g (0.02 mole) of methyl α-bromo-α-cyanoacetate in 50 ml THF at 27°. When the addition was complete the mixture was stirred for an additional hour at 27°, and then filtered to separate the solid product. Recrystallization of the crude product from chloroform-acetonitrile gave 5.8 g (95%) of the ylide hydrobromide: mp 152-153° (dec.); ir (KBr) 3040 (C-H), 2680 (C≡N), and 1735 cm^{-1} (C=O); Proton nmr (DMSO-d_6) δ 7.9 (s,2H), δ 3.88 (s,6H), δ 3.72 (s,3H).

Anal. Calculated for $C_9H_{12}N_3O_2SBr$: C, 35.30; H, 3.49; N, 13.70; S, 10.50. Found: C, 35.40; H, 3.97; N, 13.77; S, 10.49.

1,3-Dimethylimidazole-2-Thione S-Carbomethoxycyanomethylide (7a,y)

A solution of 2.28 g (0.02 mole) of DABCO in 20 ml anhydrous methanol was added to a solution of 6a,y (6.12 g, 0.02 mole) in 50 ml

anhydrous methanol and 50 ml anhydrous methylene chloride at 27°. When the addition was complete the reaction mixture was stirred for an additional 30 minutes at 27°. The solution was cooled to -30° and allowed to stand 12 hours. The crystals which separated were collected by filtration and recrystallized from methanol-methylene chloride to yield 3.9 g (87%) of the ylide: mp 128° (dec.); ir ($CHCl_3$) 3090 (C-H), 2150 (C≡N) and 1625 cm^{-1} (C=O); Proton nmr ($CDCl_3$) δ 7.68 (s,2H), δ 3.93 (s,6H), δ 3.40 (s,3H); Carbon-13 nmr (DMSO-d_6) δ 169.28 (s), δ 144.10 (s), δ 125.89 (s), δ 122.98 (s), δ 49.15 (s), δ 35.98 (s), δ 34.53 (s); Osmotic molecular weight 223.0.

Anal. Calculated for $C_9H_{11}N_3O_2S$: C, 48.00; H, 4.81; N, 18.65; S, 14.20. Found: C, 47.86; H, 4.94; N, 18.60; S, 14.14.

1,1,3,3-Tetramethyl-2-Thiourea S-Carbomethoxycyanomethylide Hydrobromide (6b,y)

1,1,3,3-Tetramethyl-2-thiourea (2.64 g, 0.02 mole) in 70 ml dry THF was added dropwise to 3.56 g (0.02 mole) methyl α-bromo-α-cyanoacetate in 50 ml THF at 27°. When the addition was complete the mixture was stirred for an additional hour at 27° and filtered to collect the crude product. Recrystallization of the solid from chloroform-acetonitrile yielded 5.8 g (94%) of the ylide hydrobromide: mp 125-126° (dec.); ir (KBr) 3035 (C-H) and 1710 cm^{-1} (C=O); Proton nmr ($CDCl_3$) δ 6.90 (s, 2H), δ 3.70 (s,3H), δ 3.52 (s,12H).

Anal. Calculated for $C_9H_{16}BrN_3O_2S$: C, 34.80; H, 5.16; N, 13.55; S, 10.32; Br, 25.80. Found: C, 34.67; H, 5.28; N, 13.50; S, 10.78;

Br, 25.69.

1,1,3,3-Tetramethyl-2-Thiourea S-Carbomethoxycyanomethylide (7b,y)

A solution of 2.24 g (0.02 mole) of DABCO in 25 ml anhydrous methylene chloride was added dropwise over a 15 minute period to a solution of 6.2 g (0.02 mole) of 6b,y in 150 ml methylene chloride maintained at 5°. When the addition was complete the mixture was allowed to stir for 30 minutes at 5° and then 50 ml of diethyl ether was added. The DABCO hydrobromide which separated was collected by filtration. The filtrate was evaporated to dryness and recrystallized from methanol-ether to give 4.1 g (89%) of the ylide as colorless cubes: mp 109-110° (dec.); ir ($CHCl_3$) 2940 (C-H), 2150 (C≡N), 1660 (C=O) and 1580 cm^{-1} (iminium); Proton nmr ($CDCl_3$) δ 3.60 (s,1H), δ 3.3 (s,4H); Osmotic molecular weight 229.0.

Anal. Calculated for $C_9H_{15}N_3O_2SBr$: C, 47.10; H, 6.60; N, 18.30; S, 13.98. Found: C, 47.19; H, 6.60; N, 18.38; S, 13.92.

1,1,3,3-Tetramethyl-2-Thiourea S-Fluorenylide Hydrobromide (6b,w)

1,1,3,3-Tetramethyl-2-thiourea (2.6 g, 0.02 mole) in 50 ml anhydrous THF was added dropwise to a solution of 9-bromofluorene (4.9 g, 0.02 mole) in 100 ml anhydrous THF at 27°. When the addition was complete the reaction mixture was stirred for one hour and then cooled to -30°. The crystals which has separated were collected by filtration and the crude product was recrystallized from THF-methanol to afford 7.2 g

(95% of the ylide hydrobromide: mp 204-206° (dec.); ir (KBr) 3025 (C-H), 1620 (iminium) and 740 cm^{-1}; Proton nmr (DMSO-d_6) δ 7.2-8.1 (m, 8H), δ 6.0 (s,1H) and δ 2.94 (s,12H).

Anal. Calculated for $C_{18}H_{21}N_2SBr$: C, 47.26: H, 5.56; N, 7.42; S, 8.48; Br, 21.04. Found: C, 57.19; N, 5.70; N, 7.30; S, 8.46; Br, 21.20.

Deprotonation of 1,1,3,3-Tetramethyl-2-Thiourea S-Fluorenylide Hydrobromide (6b,w)

Lithium diisopropyl amide (1.07 g, 0.01 mole) in 75 ml anhydrous THF was added dropwise to a suspension of 6b,w (3.77 g, 0.01 mole) in 200 ml anhydrous THF maintained at -78°. After the first few drops of base was added the solution became red and when the addition was complete the red color persisted as long as the solution was held at -78°. On warming to -35° the solution turned from red to orange-yellow. This orange-yellow color persisted even at room temperature. The solvent was evaporated on a rotary evaporator to give an orange waxy mass which was extracted with 100 ml 1:1 pentane-ether. The extract was evaporated to give an orange-red solid which was recrystallized from hexane to yield 0.9 g of red needles mp 182-184°. Mixed melting point with bisfluorenylidene showed no depression and the ir of the isolated sample was identical with that of an authentic sample of bisfluorenylidene. The remainder of the reaction mixture was washed with 10 ml water and recrystallized from benzene-methanol to give 0.8 g of 1,1,3,3-tetramethyl-2-thiourea (mp 76-78°) which was identified by comparison with an authentic sample.

1,3-Dimethylimidazole-2-Thione S-Fluorenylide Hydrobromide (6a,w)

1,3-Dimethylimidazole-2-thione (2.56 g, 0.02 mole) in 100 ml anhydrous THF was added dropwise to a solution of 9-bromofluorene (4.9 g, 0.02 mole) in 100 ml anhydrous THF at 27°. When the addition was complete the reaction mixture was stirred for one hour at 27° and then cooled to -30°. The crystals which separated were collected by filtration and the crude product was recrystallized from chloroform-methanol to yield 7.3 g (98%) of the ylide hydrobromide as colorless needles: mp 187-190° (dec.); ir (KBr) 3010 (C-H), 1240 (imidazolium) and 735 cm^{-1}; Proton nmr (DMSO-d_6) δ 8.08 (s,2H), δ 7.2-8.1 (m,8H), δ 6.0 (s,1H), and δ 3.7 (s,6H).

Anal. Calculated for $C_{18}H_{17}N_2SBr$: C, 57.91; H, 4.56; N, 7.51; S, 8.58; Br, 21.45. Found: C, 58.05; H, 4.52; N, 7.44; S, 8.50; Br, 21.60.

Deprotonation Of 1,3-Dimethylimidazole-2 Thione S-Fluorenylide Hydrobromide (6a,w)

Lithium diisopropylamide (1.07 g, 0.01 mole) in 75 ml anhydrous THF was added dropwise to a suspension of 6a,w (3.73 g, 0.01 mole) in 200 ml anhydrous THF maintained at -78°. After the first few drops of base had been added the reaction mixture became red. When the addition was complete the reaction mixture was a deep red color. The red color persisted upon warming to -25° above which temperature the solution faded to an orange-yellow color which persisted at room temperature. The

solvent was removed on a rotary evaporator to give an orange solid. This solid was extracted with 100 ml pentane-ether. The extract was evaporated to give an orange solid which was recrystallized from hexane to provide 1.1 g of red needles which were shown to be bisfluorenylidene by mixed melting point (mp 182-184°) and ir comparison. The remainder of the reaction mixture was recrystallized from 30 ml of water to give 1.2 g of 1,3-dimethylimidazole-2-thione (mp 181-182°) which was identified by comparison with an authentic sample.

1,1,3,3-Tetramethyl-2-Thiourea S-Anthronylide Hydrobromide (6b,y)

1,1,3,3-Tetramethyl-2-thiourea (2.64 g, 0.02 mole) in 20 ml anhydrous THF was added dropwise over a 10 minute period to a solution of 5.46 g (0.02 mole) of 9-bromoanthrone in 150 ml anhydrous THF at 27°. When the addition was complete the reaction mixture was stirred for an additional hour at 27° and filtered. The solid product was recrystallized from chloroform-methanol to give 7.9 g (97%) of the ylide hydrobromide as yellow needles: mp 180-182° (dec.); ir (KBr) 3020 (C-H), 1600 (iminium) and 750 cm^{-1}; Proton nmr (DMSO-d_6) δ 7.42-8.85 (m,5H) and δ 2.95 (s,12H).

Anal. Calculated for $C_{19}H_{21}N_2OSBr$: C, 56.25; H, 5.18; N, 6.91; S, 7.89; Br, 19.75. Found: C, 56.35; H, 5.11; N, 6.82; S, 7.76; Br, 19.77.

Deprotonation Of 1,1,3,3-Tetramethyl-2-Thiourea S-Anthronylide Hydrobromide (6a,v)

DABCO (2.24 g, 0.02 mole) in 15 ml anhydrous THF was added dropwise over a 15 minute period to a suspension of 8.1 g (0.02 mole) of 6a,v in 150 ml anhydrous THF maintained at -78°. The solid (3.75 g) was identified as DABCO hydrobromide [mp 285-290° (dec.)] by comparison with an authentic sample. The filtrate was allowed to warm and the blood-red color persisted up to -15° at which point the solution deposited a brown powder. The brown powder was separated by filtration and recrystallized from glacial acetic acid to give .67 g of bianthrone (mp 256-258°) which was identified by comparison with an authentic sample prepared by the method of V. V. Kozlov.[26] The mother liquor was evaporated and recrystallized from benzene-methanol to give 1.9 g of 1,1,3,3-tetramethyl-2-thiourea (mp 76-78°) which was identified by comparison with an authentic sample. A second reaction was carried out as before except 30 ml of anhydrous pyridine was added to the reaction before the addition of DABCO began. With the inclusion of pyridine in the reaction mixture the blood-red color persisted up to +10° above which point the above reaction products formed.

1,3-Dimethylimidazole-2-Thione S-Carboethoxyphenymethylide Hydrobromide (6a,u)

1,3-Dimethylimidazole-2-thione (12.8 g, 0.1 mole) in 75 ml anhydrous THF was added dropwise to a solution of 24.3 g (0.1 mole) of ethyl α-bromo-α-phenylacetate in 100 ml anhydrous THF at 27°. After the

addition was complete the reaction mixture was stirred for an additional 30 minutes. One hundred ml of hexane was added to the reaction mixture and the solid product was isolated by cooling to -30° and collected by filtration. Recrystallization from chloroform-hexane afforded 36.0 (97%) of the ylide hydrobromide as colorless needles: mp 182° (dec.); ir ($CHCl_3$) 2940 (C-H), 1740 (C=O) and 1245 cm^{-1}; Proton nmr ($CDCl_3$) δ 8.18 (s,2H), δ 7.38 (s,5H), δ 5.40 (s,1H), δ 4.23 (q,4H), δ 3.83 (s,6H), and δ 1.12 (t,6H).

Anal. Calculated for $C_{15}H_{19}N_2O_2SBr$: C, 48.52; H, 5.12; N, 7.55; S, 8.63; Br, 21.56. Found: C, 48.55; H, 5.19; N, 7.49; S, 8.66; Br, 21.48.

Deprotonation Of 1,3-Dimethylimidazole-2-Thione S-Carboethoxyphenylmethylide Hydrobromide (6a,u)

Lithium diisopropylamide (2.14 g, 0.02 mole) in 75 ml anhydrous THF was added dropwise to a solution of 7.42 g (0.02 mole) of 6a,u in 100 ml anhydrous THF maintained at -78°. When the addition was complete the cloudy solution was a light yellow color. On warming the solution became colorless at -20°. The solvent was removed on a rotary evaporator and the residual waxy white solid was extracted two time with 100 ml portions of diethyl ether. The combined extracts were concentrated to an oil which was subjected to distillation in vacuo. The distillate was divided into two fractions. The fraction $bp_{1.0}$ 160-165° crystallized giving 630 mg of a solid (mp 50-53°) and the fraction, $bp_{1.0}$ 170-180°, also crystallized giving 420 mg of a solid (mp 60-68°). Both samples were recrystallized to give two samples weighing 520 mg and 370 mg

(mp 52-54° and 77-78°), respectively. The first solid (mp 52-54°) was identified as diethyl diphenylmaleate by mixture melting point comparison with an authentic sample synthesized according to Mme. Ramart-Lucas and J. Hock.[27] Photolysis of the authentic diethyl diphenylmaleate in THF (Hg-quartz) yielded a sample of diethyl diphenylfumarate which was identical with the second solid (mp 77-78°). Conversion of both the esters to the corresponding fumaric acid and maleic anhydride provided further structure conformation.[27]

The diethyl ether insoluble portion was recrystallized from water to give 2.0 g of the 1,3-dimethylimidazole-2-thione mp 180-183° which was identified by comparison with an authentic sample.

1,3-Dimethylimidazole-2-Thione S-p-Toluensulfonimide

1,3-Dimethylimidazole-2-thione (12.8 g, 0.1 mole) was added in a single portion to a solution of 28.2 g (0.1 mole) of Chloramine-T trihydrate in 200 ml anhydrous methanol at 27°. The mixture was stirred for two hours and then diluted with 75 ml anhydrous methylene chloride. The reaction mixture was then filtered through celite to remove the precipitated sodium chloride. The filtrate was cooled to -78° and the crystalline product which separated was collected by filtration. The crude material was recrystallized from methanol to give 28.0 g (94%) of the thione S-imide as colorless plates: mp 185-190° (dec.); ir (KBr) 3090 (C-H), 1260 and 900 cm^{-1}; Proton nmr (DMSO-d_6) δ 7.53 (s,2H), δ 7.28 (q,rH), δ 3.75 (s,6H), and δ 2.25 (s,3H); Carbon-13 nmr (DMSO-d_6) δ 147.1 (s), δ 143.00 (s), δ 122.92 (s), δ 35.49 (s), and δ 20.75 (s);

Osmotic molecular weight ($CHCl_3$) 299.0.

Anal. Calculated for $C_{12}H_{15}N_3O_2S_2$: C, 48.48; H, 5.00; N, 14.14; S, 21.55. Found: C, 48.25; H, 5.14; N, 14.09; S, 21.38.

Dimethylsulfonium Dicyanomethylide

A sample of dimethylsulfonium dicyanomethylide was prepared by the procedure of W. J. Middleton[27] using method "C". Recrystallization of the crude product from isopropyl alcohol gave white prisms: mp 98-100° (lit.[27] 99-100°).

2-Methylmercapto-1,3-Dimethylimidazolium-Iodide (17)

Methyl iodide (14.2 g, 0.1 mole) was added dropwise to a solution of 12.8 g (0.01 mole) of 1,3-dimethylimidazole-2-thione in 100 ml anhydrous methylene chloride at 27°. The precipitated product was collected by filtration under inert atmosphere and recrystallized from methanol-methylene chloride to give 26.3 g (97%) of the iodide as colorless cubes: mp 187° (dec.); Proton nmr (DMSO-d_6) δ 7.98 (s,2H), δ 3.97 (s,6H), and δ 2.58 (s,3H; Carbon-13 nmr (DMSO-d_6) δ 140.82 (s); δ 124.49 (s), δ 36.47 (s), and δ 17.71 (s); ir (KBr) 3040 (C-H) and 1260 cm^{-1}.

Anal. Calculated for $C_6H_{11}N_2SI$: C, 26.66; H, 4.07; N, 10.30; S, 11.85. Found: C, 26.61; H, 4.08; N, 10.36; S, 11.90.

S-Methyl-1,1,3,3-Tetramethyl-2-Thiourea Iodide (18)

Methyl iodide (14.2 g, 0.1 mole) was added dropwise to a solution of 13.2 g (0.1 mole) of 1,1,3,3-tetramethyl-2-thiourea in 75 ml anhydrous methylene chloride and 25 ml anhydrous diethyl ether at 27°. When the addition was complete the reaction mixture was cooled to -30° and filtered under inert atmosphere. The crude product was recrystallized from chloroform-acetonitrile to give 26.1 g (95%) of the iodide as colorless needles: mp 179-181° (dec.); ir (KBr) 3000 (C-H), 1595 (iminium) and 1385 cm^{-1}; Proton nmr (DMSO-d_6) δ 3.17 (s,12H) and δ 2.61 (s,3H); Carbon-13 nmr (DMSO-d_6) δ 174.55 (s), δ 43.56 (s), and δ 16.93 (s).

Anal. Calculated for $C_6H_{15}N_2SI$: C, 26.28; H, 5.47; N, 10.22; S, 11.68. Found: C, 26.22; H, 5.46; N, 10.26; S, 11.63.

10-Methylthioacridone

10-Methylthioacridone was prepared by a modification of the procedure by Glen and Schaarschmidt.[29] Methyl iodide (14.2 g, 0.1 mole) was added dropwise to a solution of 21.4 g (0.1 mole) of 9-chloroacridine in 100 ml anhydrous THF at 27°. When the addition was complete the mixture was allowed to stir for 12 hours at 27°. The THF was removed on a rotary evaporator and replaced with 400 ml anhydrous ethanol. Sodium sulfide nonahydrate (24.0 g, 0.1 mole) was added in a single portion. The mixture was allowed to stir at 27° for 48 hours. The ethanol was removed on a rotary evaporator and the red-brown solid was washed twice with 100 ml portions of water and then dried in vacuo. The crude solid was recrystallized from isopropanol to yield 15.2 g (67%) of the thione

as red needles: mp 262-265° (lit.[29] 263°).

Reaction Of Dimethyl Acetylenedicarboxylate With 1,3-Dimethylimidazole-2-Thione S-Dicarboethoxymethylide (7a,z)

Dimethyl acetylenedicarboxylate (1.0 g, 0.01 mole) in 10 ml anhydrous THF was added dropwise to 286.g (0.01 mole) of 7a,z in 50 ml of anhydrous THF at 27°.

When the addition was complete the mixture was stirred for an additional two hours. The THF was removed on a rotary evaporator to leave a brown intractable mass. TLC (silica, $CHCl_3$-ether) showed at least 10 products. The mixture was discarded when no products could be isolated.

Thermal Decomposition of 1,3-Dimethylimidazole-2-Thione S-Dicyanomethylide (7a,x)

A solution of 1,3-dimethylimidazole-2-thione S-dicyanomethylide (1.92 g, 0.01 mole) in 50 ml chloroform was refluxed for 30 minutes. Upon heating the solution turned a blue-black color. After evaporation of the solvent a black solid remained. The solid was sublimed in vacuo (.05 mm Hg) to yield an initial colorless sublimate. The sublimation was discontinued when the sublimate began to turn blue. The sublimate was then removed and recrystallized from 1,3-dibromoethane to give 84 mg of a solid mp 200-204°. The solid was identified as tetracyanoethylene (TCNE) by comparison with an authentic sample. The sublimand was extracted with 50 ml hot water and treated with decolorizing carbon. When the extracts were cooled they deposited light blue crystals, mp

170-178°. Repeated water recrystallizations afforded 700 mg of 1,3-dimethylimidazole-2-thione which was identified by comparison with an authentic sample.

The thermal decomposition was also carried out in refluxing benzene and in refluxing cyclohexene in order to trap any dicyanocarbene present, but these attempts failed and the only products which could be isolated were TCNE and imidazolethione. Attempts to trap dicyanocarbene with dialkyl or diaryl sulfides also met with no success. The crude reaction material in all cases was subjected to analysis by proton nmr and no carbene addition products were observed. The blue color of the reaction mixtures was traced to the charge transfer complex between TCNE and the imidazolethione.

Photolytic Decomposition Of 1,3-Dimethylimidazole-2-Thione S-Dicyanomethylide (7a,x)

A solution of 1,3-dimethylimidazole-2-thione S-dicyanomethylide (1.92 g, 0.01 mole) in 300 ml anhydrous THF at 25° was subjected to photolysis through a quartz probe with a 250-w high pressure Hg-discharge Hanovia lamp. After three hours of photolysis the THF solution had become a brilliant blue. The solvent was removed on a rotary evaporator and the solid residue was subjected to fractional sublimation. Sublimation was discontinued when the sublimate began to turn blue. The sublimate was recrystallized from 1,2-dibromoethane to give 92 mg of TCNE which was identified by comparison with an authentic sample. The sublimand was recrystallized from water several times to give 1.0 g of 1,3-dimethylimidazole-2-thione mp 181-182° which was identified by comparison

with an authentic sample. The photolysis was also conducted with added alkenes and dialkyl sulfides in hopes of trapping dicyanocarbene, but the only products which could be isolated from these reactions were TCNE and imidazolethione. Proton nmr of the crude reaction mixtures provided no evidence for the presence of carbene addition products.

Thermal Decomposition of 1,1,3,3-Tetramethyl-2-Thiourea S-Dicyanomethylide (7b,x)

A solution of 1,1,3,3-tetramethyl-2-thiourea S-dicyanomethylide (1.96 g, 0.01 mole) in 50 ml anhydrous methylene chloride was refluxed for two hours under an inert atmosphere, after which the reaction became a blue-black color. The methylene chloride was removed on a rotary evaporatory to give a black solid. By TLC (silica, chloroform-ethanol) the solid was shown to contain both TCNE and tetramethylthiourea. The 1,1,3,3-tetramethyl-2-thiourea was isoltated from the black reaction residue by sublimation in vacuo. The crude thiourea was recrystallized from benzene-ethanol to give 750 mg of tetramethylthiourea (mp 73-75°) which was identified by comparison with an authentic sample. The sublimand was dissolved in hot 1,3-dibromoethane and treated with charcoal to give on cooling 85 mg of TCNE which was identified by comparison with an authentic sample. As with the imidazole ylide attempts to trap dicyanocarbene with alkenes and dialkyl sulfides failed.

Thermal Decomposition Of 1,3-Dimethylimidazole-2-Thione S-Dicarboethoxymethylide (7a,z)

1,3-Dimethylimidazole-2-thione S-dicarboethoxymethylide (2.86 g, 0.01 mole) was dissolved in 60 ml carbon tetrachloride and refluxed for six hours. The reaction course was followed by TLC (silica, chloroform-ethanol) and terminated when the starting ylide had been consumed. The final TLC showed only two major products which were tentatively identified as tetraethyl ethylenetetracarboxylate and 1,3-dimethylimidazole-2-thione. The crude reaction mixture was extracted twice with 20 ml portions of hot water. The aqueous extracts were combined and reduced to 20 ml volume on a rotary evaporator. When cooled to 0° the solution deposited 1.1 g of 1,3-dimethylimidazole-2-thione which was identified by comparison with an authentic sample. The oil remaining from the original reaction mixture was dissolved in warm ethanol and cooled to -30°. The precipitated white solid (0.4 g, mp 51-53°) was collected by filtration. This solid was identified as tetraethyl ethylenetetracarboxylate by mixture melting point comparison with an authentic sample.[30] Attempts to trap carbene intermediates were made by conducting the decomposition in the presence of alkenes or dialkyl sulfides. Proton nmr analysis of the reactions showed only two products in all cases, tetraethyl ethylenetetracarboxylate and 1,3-dimethylimidazole-2-thione.

Photolytic Decomposition of 1,3-Dimethylimidazole-2-Thione S-Dicarboethoxymethylide (7a,z)

A THF solution of 1,3-dimethylimidazole-2-thione S-dicarboethoxymethylide (2.86 g, 0.01 mole) was irradiated for 12 hours with a quartz

probe (high pressure Hg-discharge 250-w Hanovia lamp). The solvent was evaporated and the residue examined by proton nmr to reveal only two products present, 1,3-dimethylimidazole-2-thione and tetraethyl ethylenetetracarboxylate. These products were isolated in the same manner as in the thermolysis reaction to give 200 mg of tetraethyl ethylenetetracarboxylate and 1.0 g of 1,3-dimethylimidazole-2-thione (both materials were identified by comparison with authentic samples). As in all the other decompositions no evidence was found for carbene intermediates by trapping experiments.

Thermal Decomposition of 1,1,3,3-Tetramethyl-2-Thiourea S-Dicarboethoxymethylide (7b,z)

A solution of 1,1,3,3-tetramethyl-2-thiourea S-dicarboethoxymethylide (2.9 g, 0.01 mole) in 100 ml toluene was refluxed for eight hours. The reflux was discontinued when the starting ylide had been consumed (TLC, silica, chloroform-ether).

The toluene was removed on a rotary evaporator and the residue, which contained only two materials by TLC and proton nmr analysis, was dissolved in a minimum volume of warm ethanol. On cooling to 0° 94 mg of tetraethyl ethylenetetracarboxylate (mp 51-53°) separated as colorless needles. Further cooling of the filtrate to -78° afforded impure 1,1,3,3-tetramethyl-3-thiourea (mp 70-75°). Recrystallization of the crude thiourea from benzene-ethanol afforded 1.0 g of the pure material (mp 73-75°). Again, trapping experiments failed to provide evidence for carbene intermediates.

Thermal Decomposition Of 1,3-Dimethylimidazole-2-Thione S-Carbomethoxycyanomethylide (7a,y)

1,3-Dimethylimidazole-2-thione S-carbomethoxycyanomethylide (2.25 g, 0.01 mole) in 75 ml chloroform was refluxed for 30 minutes. The reaction mixture became dark brown and the solvent was removed on a rotary evaporator. The residue showed several non-origin products on TLC (silica, chloroform-hexane). The residue was extracted with two 50 ml portions of hot water. The water extracts were treated with charcoal and reduced to 50 ml total volume on a rotary evaporator and after cooling to 5° the aqueous extracts deposited 1.0 g of 1,3-dimethylimidazole-2-thione. The light tan crystals which remained after the water extractions were recrystallized to give 0.2 g of dimethyl dicyanofumarate (mp 178-180°) which was identified by comparison with an authentic sample.[31,32,34] Again, this decomposition was shown to be free from carbene intermediates.

Photolytic Decomposition Of 1,3-Dimethylimidazole-2-Thione S-Carbomethoxycyanomethylide (7a,y)

The photolytic decomposition was conducted with 2.25 g (0.01 mole) of 1,3-dimethylimidazole-2-thione S-carbomethoxycyanomethylide in 300 ml anhydrous THF with a high pressure Hg-discharge Hanovia lamp. After six hours the photolysis was discontinued and the THF removed on a rotary evaporator. The crude reaction mixture was treated as in the thermolysis and provided 1.2 g of imidazolethione and 0.23 g of dimethyl dicyanofumarate. This decomposition was also free of carbene

intermediates.

Ylide-Thione Exchange Between 1,3-Dimethylimidazole-2-Thione S-Dicarboethoxymethylide (7a,z) and 1,1,3,3-Tetramethyl-2-Thiourea

1,3-Dimethylimidazole-2-thione S-dicarboethoxymethylide (2.86 g, 0.01 mole) was dissolved in 60 ml anhydrous methylene chloride and 1.32 g (0.01 mole) of 1,1,3,3-tetramethyl-2-thiourea was added in a single portion. The mixture was stirred at 27° for 12 hours. The methylene chloride was removed on a rotary evaporator. The residual white solid was dissolved in methanol at 27° and diethyl ether was added until the solution became cloudy. The mixture was allowed to stand at 5° for six hours and was then filtered. The solid which was collected (1.4 g) was identified as 1,1,3,3-tetramethyl-2-thiourea S-dicarboethoxymethylide (mp 104-105°) by comparison with an authentic sample. 1,3-Dimethylimidazole-2-thione was isolated from the filtrate by evaporation of solvent and recrystallization from water to give 1.0 g of the pure material.

The reaction between tetramethylthiourea and 1,3-dimethylimidazole-2-thione S-dicyanomethylide proceeded immediately upon mixing at room temperature in chloroform solution, however, attempted isolation of the 1,1,3,3-tetramethyl-2-thiourea S-dicyanomethylide resulted in decomposition. The course of the reaction was easily followed by proton nmr since all the reactants and products have varied chemical shifts.

In no case of ylide-thione exchange was 1,3-dimethylimidazole-2-thione able to replace a tetramethylthiourea moiety incorporated in an ylide.

The transfer of a methylide group to pyridine could not be achieved with any of the ylides described in this work. Transfer of a methylide group to dimethyl sulfide was an extremely slow process usually taking more than a week as detected by proton nmr.

An exchange between tetramethylthiourea and 1,3-dimethylimidazole-2-thione S-p-toluenesulfonimide was also observed and 1,1,3,3-tetramethyl-2-thiourea S-p-toluenesulfonimide[8] could be isolated as a product.

Ylide-Ylide Exchange Between 1,3-Dimethylimidazole-2-Thione S-Dicyanomethylide And 1,1,3,3-Tetreamethyl-2-Thiourea S-Dicarboethoxymethylide

The reaction between 1,3-Dimethylimidazole-2-thione S-dicyanomethylide and tetramethyl-2-thiourea S-dicarboethoxymethylide could be conveniently followed by proton nmr signals. The reaction had reached equilibrium in chloroform-d_1 after 30 minutes giving a solution of four ylides. The two starting materials were present along with 1,3-dimethylimidazole-2-thione S-dicarboethoxymethylide and 1,1,3,3-tetramethyl-2-thiourea S-dicyanomethylide. After 30 minutes there was significant decomposition of the tetramethylthiourea-dicyanomethylide to TCNE and tetramethylthiourea. The ultimate reaction products after one hour were 1,3-dimethylimidazole-2-thione S-dicarboethoxymethylide, 1,1,3,3-tetramethyl-2-thiourea and TCNE.

A mixture of 1.92 g (0.01 mole) of 1,3-dimethylimidazole-2-thione S-dicyanomethylide and 2.9 g (0.01 mole) of 1,1,3,3-tetramethyl-2-thiourea S-dicarboethoxymethylide in 50 ml anhydrous methylene chloride

was allowed to stir at 27° for 45 minutes. After the solvent was removed by evaporation products were isolated by chromatography, (silica, methylene chloride-methanol) and identified by comparison with authentic samples: 1,3-dimethylimidazole-2-thione S-dicyanomethylide (0.2 g); 1,3-dimethylimidazole-2-thione S-dicarboethoxymethylide (0.9 g); 1,1,3,3-tetramethyl-2-thiourea (1.1 g); and TCNE (84 mg).

Ylide exchanges between simple sulfonium ylides and thione S-methylides were extremely slow reactions and when the progress was monitored by proton nmr, products were detectable only after several days. By proton nmr exchange between 1,3-dimethylimidazole-2-thione S-carbomethoxycyanomethylide and dimethylsulfonium dicyanomethylide could be observed as a slow process, but attempts to isolate ylide products failed because of their instability.

1,3-Dimethylimidazole-2-Thione S-Dicarboethoxymethylide with TCNE

TCNE (2.56 g, 0.02 mole) and 1,3-dimethylimidazole-2-thione S-dicarboethoxymethylide (2.86 g, 0.01 mole) were suspended in 50 ml of anhydrous methanol and the mixture was stirred for 20 minutes at 27° then filtered to remove the excess TCNE.

The filtrate was cooled to -30° and after one hour had deposited crystals (1.5 g, mp 90-94°) of impure 1,3-dimethylimidazole-2-thione S-dicyanomethylide. The impure product was recrystallized from methanol to give 1.1 g of pure 1,3-dimethylimidazole-2-thione S-dicyanomethylide (mp 96°) which was identified by comparison with an authentic sample.

1,3-Dimethylimidazole-2-Thione S-Dicarboethoxymethylide And Malononitrile

Malononitrile (1.32 g, 0.02 mole) was added as a single portion to 1.43 g (0.005 mole) of 1,3-dimethylimidazole-2-thione S-dicarboethoxymethylide in 100 ml anhydrous methylene chloride. The solution was stirred at room temperature while the reaction progress was followed by TLC (silica, methylene chloride-methanol). After 30 minutes the reaction mixture had become noticably yellow but TLC failed to show any 1,3-dimethylimidazole-2-thione S-dicyanomethylide. Two drops of anhydrous triethylamine were added as a catalysis and after one hour TLC showed the presence of the dicyano ylide, 7a,x, as well as several unidentified by-products. After 6 hours all the diester ylide had been consumed and the only ylide evidenced by TLC was the dicyano ylide, 7a,x. The presence of many by-products prevented the isolation of the unstable dicyano ylide. This same reaction was carried out in $CDCl_3$ in an nmr tube and the nmr spectrum of the dicyano ylide was observed after several hours.

2,2'-Bis(1,3-Dimethylimidazolium)disulfide Dibromide (34)

Bromine (8.0 g, 0.05 mole) in 15 ml anhydrous methylene chloride was added dropwise to a solution of 12.8 g (0.1 mole) of 1,3-dimethylimidazole-2-thione in 75 ml anhydrous methylene chloride maintained at 0°. When the addition was complete the precipitated solid was collected by filtration and recrystallized from ethanol-chloroform to give 19.5 g (94%) of the disulfide as yellow crystals: mp 240° (dec.); ir (KBr) 3040 (C-H), 1500, 1250 (imidazolium) and 785 cm^{-1}; Proton nmr (DMSO-d_6)

δ 7.92 (s,2H) and δ 4.03 (s,6H).

Anal. Calculated for $C_{10}H_{16}N_4S_2Br_2$: C, 28.85; H, 3.85; N, 13.46; S, 15.38; Br, 38.46. Found: C, 28.63; H, 3.95; N, 13.38; S, 15.26; Br, 38.26.

S,S-Dibromo-1,3-Dimethylimidazole-2-Thione (31)

Bromine (16.0 g, 0.1 mole) in 30 ml anhydrous methylene chloride was added dropwise to a solution of 12.8 g (0.1 mole) of 1,3-dimethylimidazole-2-thione in 50 ml anhydrous methylene chloride maintained at 0°. After half the bromine had been added the reaction mixture was a suspension of the disulfide, 34, as the addition continued the solid began to dissolve and solution became orange. When the addition was complete the solution was allowed to warm to 27° and stir for 20 minutes. On cooling to -30° and filtering the solution yielded 26.3 g (91%) of the dibromide. A sample of the dibromide was recrystallized from methylene chloride and had: mp 173° (dec.); ir (KBr) 3060 (C-H), 1235 (imidazolium) and 760 cm^{-1}; Proton nmr ($CDCl_3$) δ 7.22 (s,2H) and 3.47 (s,6H); Carbon-13 nmr ($CDCl_3$) 121.89 (s) and 36.89 (s); Osmotic molecular weight ($CHCl_3$) 282.0.

Anal. Calculated for $C_5H_8N_2SBr_2$: C, 20.88; H, 2.78; N, 9.72; S, 11.11; Br, 55.56. Found: C, 20.81; H, 2.81; N, 9.80; S, 11.14; Br 55.41.

2,2'-Bis(1,3-Dimethylimidazolium)disulfide Dibromide (34) from 1,3-Dimethyl-2-Thione (4a) And S,S-Dibromo-1,3-Dimethylimidazole-2-Thione (31)

1,3-Dimethylimidazole-2-thione (1.28 g, 0.01 mole) was added as a single portion to a solution of 2.88 g (0.01 mole) of S,S-dibromo-1,3-dimethylimidazole in 70 ml anhydrous methylene chloride at 27°. The mixture was stirred for 30 minutes and filtered to give 4.1 g (99%) of 34: mp 240° (dec.).

2,2'-Bis(1,3-Dimethylimidazolium)disulfide Dichloride

Chlorine gas (3.5 g, 0.05 mole) was passed into a solution of 12.8 g (0.1 mole) of 1,3-Dimethylimidazole-2-thione in 100 ml anhydrous methylene chloride maintained at 0°. When all the chlorine had been added the solution was allowed to warm to 27° and stirred for 30 minutes. Filtration of the reaction mixture afforded 16.1 g (99%) of the disulfide as an off-white powder: mp 246° (dec.); ir (KBr) 3045 (C-H), 1505, 1250, and 790 cm^{-1}. Proton nmr (DMSO-d_6) δ 7.93 (s,2H) and δ 4.04 (s,6H).

Anal. Calculated for $C_{10}H_{16}N_4S_2Cl_2$: C, 36.70; H, 4.89; N, 17.13; S, 19.57; Cl, 21.17. Found: C, 36.80; H, 4.92; N, 17.22; S, 19.65; Cl, 20.98.

S,S-Dichloro-1,3-Dimethylimidazole-2-Thione

Chlorine gas (7.1 g, 0.1 mole) was passed into a solution of 12.8 g (0.1 mole) of 1,3-dimethylimidazole-2-thione in 100 ml anhydrous methylene chloride maintained at 0°. When the addition was complete the light yellow solution was cooled to -30° and deposited 19.1 g (96%) of

the dichlorothione: mp 157° (dec.); ir (KBr) 3055 (C-H), 1240, and 760 cm^{-1}; Proton nmr ($CDCl_3$) δ 7.22 (s,2H) and δ 4.01 (s,6H); Osmotic molecular weight ($CHCl_3$) 193.0.

Anal. Calculated for $C_5H_8N_2SCl_2$: C, 30.15; H, 4.02; N, 14.07; S, 16.08; Cl, 35.68. Found: C, 29.89; H, 4.27; N, 13.83; S, 15.85; Cl, 34.73.

S-Bromo-S-Iodo-1,3-Dimethylimidazole-2-Thione

Iodine (1.27 g, 0.005 mole) was added as a single portion to a solution of 12.8 g (0.01 mole) of 1,3-dimethylimidazole-2-thione in 40 ml anhydrous methylene chloride. The mixture was stirred until all the iodine had dissolved and was then cooled to 0°. Bromine (0.8 g, 0.005 mole) in 5 ml anhydrous methylene chloride was added dropwise to a cooled solution. The reaction mixture was warmed to 27° and stirred for 30 minutes. After cooling to -30° the reaction was filtered to give 2.8 g (84%) of the iodobromothione as orange-red crystals: mp 147-150°; ir (KBr) 3100 (C-H), 1230 (imidazolium) and 760 cm^{-1}; Proton nmr ($CDCl_3$) δ 7.72 (s,2H) and δ 3.82 (s,6H); Osmotic molecular weight 325.0.

Anal. Calculated for $C_5H_8N_2SBrI$: C, 17.91; H, 2.39; N, 8.36; S, 9.56; I, 37.91; Br, 23.88. Found: C, 17.73; H, 2.40; N, 8.33; S, 9.62; I, 37.65; Br, 23.93.

1,3-Dimethylimidazolium-2-Thiocyano Bromide (33)

Cyanogen bromide (1.06 g, 0.01 mole) in 15 ml anhydrous methylene chloride was added to a solution of 1.28 g (0.01 mole) of 1,3-dimethylimidazole-2-thione in 30 ml methylene chloride. When the addition was

complete the solid which had formed was collected by filtration and recrystallized from ethanol-methylene chloride to afford 2.1 g (90%) of the thiocyano bromide as colorless needles: mp 220° (dec.); ir (KBr) 3030 (C-H), 1245 (imidazolium) and 830 cm^{-1}; Proton nmr (DMSO-d_6) δ 8.05 (s,2H) and δ 3.97 (s,6H).

Anal. Calculated for $C_6H_8N_3SBr$: C, 30.64; H, 3.4; N, 17.87; S, 13.62; Br, 34.04. Found: C, 30.58; H, 3.46; N, 17.96; S, 13.77; Br, 34.19.

Hydrolysis Of S,S-Dibromo-1,3-Dimethylimidazole-2-Thione

S,S-Dibromo-1,3-dimethylimidazole-2-thione (2.88 g, 0.01 mole) is dissolved in 100 ml distilled water. After solution was complete, sodium bicarbonate was added cautiously in small portions until the solution was slightly basic to litmus paper. The water was slowly removed on a rotary evaporator until the volume was about 30 ml. The colorless needles which separated on cooling to 5° were collected by filtration. The solid was identified as 1,3-dimethylimidazole-2-thione: mp 181-182° (1.1 g).

CHAPTER IV

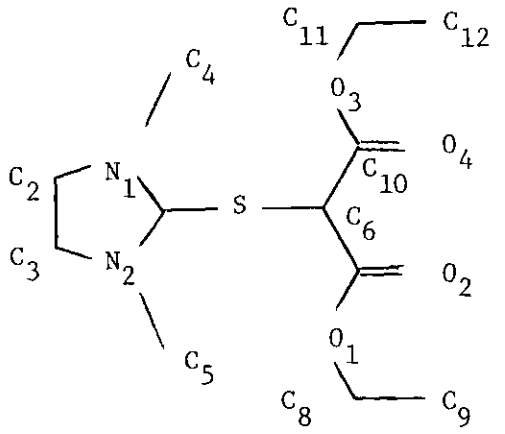
X-RAY STRUCTURES

X-Ray Structure Of 1,3-Dimethylimidazole-2-Thione S-Dicarboethoxymethylide (7a,z)

The reflection data were collected on a Picker card controlled diffractometer using MoK_{α} radiation with a Zirconium filter.

The space was determined to be $P2_{1/C}$ by consistent absences. The cell parameters were a = 8.3458, b = 14.1183, c = 15.4286, and β = 128.881. There were four molecules per unit cell.

The structure refinement was based on 718 reflections whose intensity was greater than 2 sigma. After the placement of all non-hydrogen atoms the conventional R factor was .1074 and the weighted R factor was .0763. Structure factor tables are listed in the appendix.



Using the numbering system indicated above the atomic fractional cell coordinates are listed in Table 1.

Table 1. Atmoic Fractional Cell Coordinates in 7a,z.

Atom	x	y	z
S	-.0473	.0906	.0566
N_1	.1703	-.0365	.2286
N_2	.3241	.0986	.2733
C_1	.1525	.0534	.1895
C_2	.3536	-.0406	.3371
C_3	.4418	.0444	.3629
C_4	.0186	-.1131	.1687
C_5	.3680	.2013	.2707
O1	-.2884	.0582	.1273
O2	-.3732	.2380	.1124
O3	-.0111	.2806	.0079
O4	-.1474	.3584	.9759
C6	-.1432	.1911	.0765
C7	-.2747	.1790	.1068
C8	-.4212	.0666	.1532
C9	-.3940	-.0429	.1868
C10	-.1068	.2835	.0547
C11	.0372	.3714	-.0110
C12	.1189	.3561	-.0746

Table 2. Selected Bond Lengths And Angles In 7a,z

	Bond Length, Å	Angle Degrees
$S-C_1$	1.738	
$S-C_6$	1.741	
C_1-S-C_6		104.26
C_1-N_1	1.369	
C_1-N_2	1.336	
$N_1-C_1-N_2$		107.58
N_1-C_1-S		122.31
N_2-C_1-S		129.97
C_6-C_7	1.429	
C_6-C_{10}	1.408	
$C_7-C_6-C_{10}$		121.06
C_7-C_6-S		118.87
$C_{10}-C_6$		119.87
C_7-O_1	1.371	
C_7-O_2	1.234	
$O_1-C_7-O_2$		118.32
$O_1-C_7-C_6$		113.03
$O_2-C_7-C_6$		128.65
$C_{10}-O_3$	1.372	
$C_{10}-O_4$	1.249	

Table 2. Selected Bond Lengths And Angles In 7a,z (Continued)

	Bond Length, Å	Angle Degrees
O_3-C_{10}-O_4		119.38
O_3-C_{10}-C_6		113.84
O_4-C_{10}-C_6		126.78

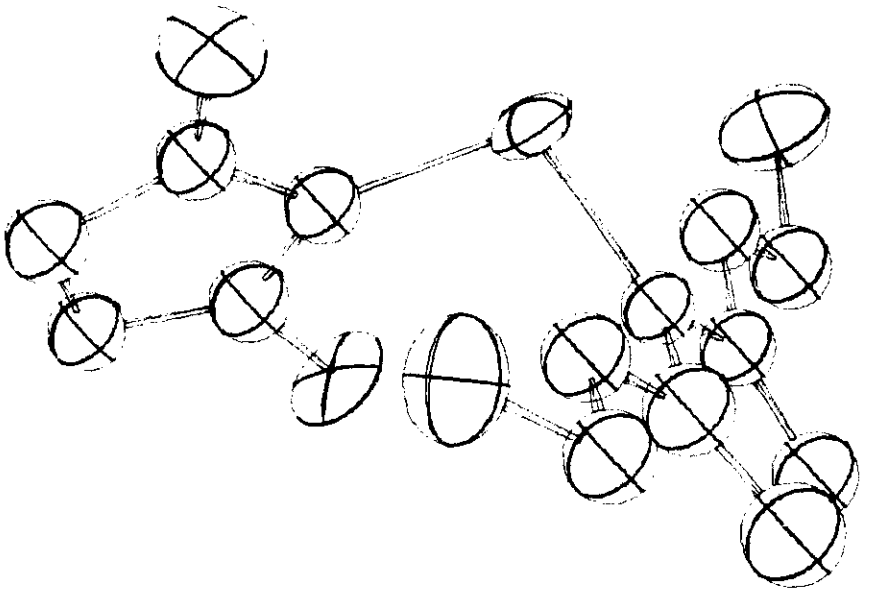
Table 3 lists Dihedral angles between planes defined by three atoms.

Table 3. Dihedral Angles In 7a,z

$(N_1C_1S)(C_1SC_6)$	58.24°
$(N_2C_1S)(C_1SC_6)$	125.95°
$(C_7C_6S)(C_1SC_6)$	78.01°
$(C_{10}C_6S)(C_1SC_6)$	106.99°

ORTEP of 1,3-Dimethylimidazole-2-Thione

S-Dicarboethoxymethylide



X-Ray Structure Of S,S-Dibromo-1,3-

Dimethylimidazole-2-Thione (31)

The reflection data were collected on a Syntex Model P_{2_1} diffractometer using MoK_{α} radiation and a graphite monochromator.

The space group was determine to be $P2_{1/C}$ by consistent absences. The cell parameters were a = 8.0182, b = 14.4624, c = 16.4209, and β = 95.530. There were eight molecules per unit cell (two non-equivalent sets).

The structure refinement was based on 1596 reflections whose intensity was above 3 sigma. After the placement of all non-hydrogen atoms the conventional R factor was 0.08 and the weighted R factor was .09 (no corrects were applied for absorption). Structure factor tables are listed in the appendix.

Using the numbering system indicated in the ORTEP on page 53 the atomic fractional cell coordinates are listed in Table 4.

Table 4. Atomic Fractional Cell Coordinates In 31

Atom	x	y	z
S	.3174	.2722	.3736
Br_1	.4982	.2181	.2599
Br_2	.1485	.3240	.4792
N_1	.5034	.4312	.3713
N_2	.4980	.3410	.4718
C_1	.4721	.2498	.4038
C_2	.6404	.4747	.4146
C_3	.4128	.4693	.2963
C_4	.6006	.2562	.5247
C_5	.6848	.4156	.4722
S'	.1819	.0561	.2935
Br_1'	.3678	.0049	.4123
Br_2'	-.0180	.1005	.1703
N_1'	-.0853	.0017	.3746

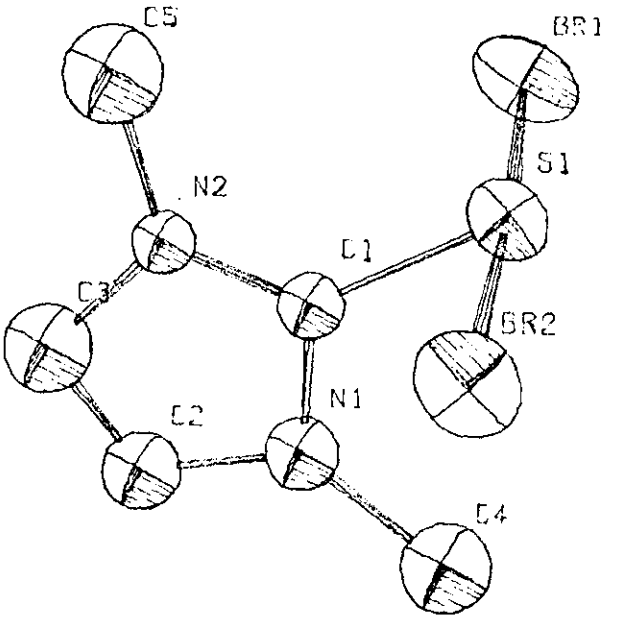
Table 4. Atomic Fractional Cell Coordinates In 31 (Continued)

Atom	x	y	z
N_2'	.0141	-.1069	.3054
C_1'	.0305	-.0222	.3216
C_2'	-.1711	-.0766	.3893
C_3'	-.1196	-.1432	.3453
C_4'	-.1107	.0975	.4075
C_5'	-.1143	-.1596	.2490

Table 5. Selected Bond Lengths And Angles In 31

	Bond Length, Å	Bond Angle, Degrees
$S-Br_1$	2.590	
$S-Br_2$	2.418	
$S-C_1$	1.713	
Br_1-S-Br_2		179.49
Br_1-S-C_1		88.13
Br_2-S-C_1		88.40
C_1-N_1	1.254	
C_1-N_2	1.376	
$N_1-C_1-N_2$		107.74
Angles between planes defined by three atoms:		
$(N_1C_1N_2)(Br_1SBr_2)$		90.0°

ORTEP Of S,S-Dibromo-1,3-Dimethylimidazole-2-Thione



X-Ray Structure of 1,3-Dimethylimidazolium

-2-Thiocyano Bromide (33)

The reflection data were collected on a Syntex Model $P2_1$ diffractometer using MoK_α radiation and a graphite monochromator.

The space group was determined to be $P2_{1/C}$ by consistent absences. The cell parameters were a = 7.288, b = 9.502, c = 15.206, and β =

122.459. There were four molecules per unit cell.

The structure refinement was based on 1248 reflections whose intensity was above 3 sigma. After the placement of all non-hydrogen atoms the conventional R factor was .043 and the weighted R factor was .049. Structure factor tables are listed in the appendix.

Using the numbering system indicated on the ORTEP on page 55 the atomic fractional cell coordinates are listed in Table 6.

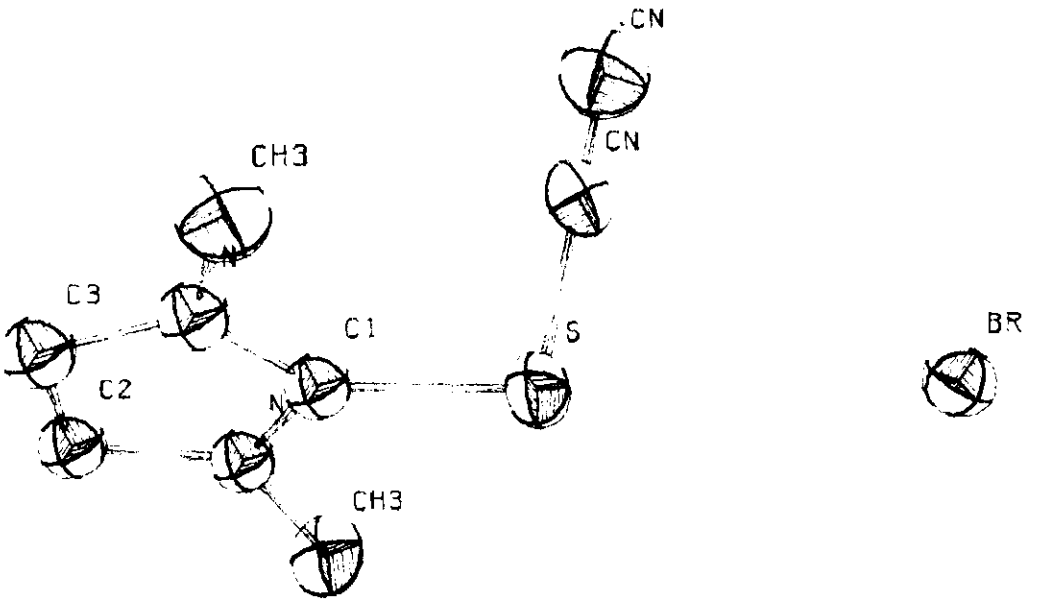
Table 6. Atomic Fractional Cell Coordinates In 33

Atom	x	y	z
S	.0476	-.1788	.1581
Br	.2564	.1285	.2587
CN1	.1742	-.1378	.0903
CN2	.2535	-.1119	.0472
N1	-.2277	-.3788	.0155
N2	.0581	-.4672	.1509
C1	-.0395	-.3480	.1053
C2	-.0674	.4213	.0922
C3	-.2474	.4797	.0057
$CH_3$1	.2627	-.4800	.2554
$CH_3$2	-.3884	-.2754	-.0574

Table 7. Selected Bond Lengths And Angles In 33

	Bond Length, Å	Angle, Degrees
$S-C_1$	1.756	
$S-CN_1$	1.757	
C_1-S-CN_1		96.20
C_1-N_1	1.349	
C_1-N_2	1.320	
$N_1-C_1-N_2$		108.24
N_1-C_1-S		125.74
N_2-C_1-S		125.75
S-Br	3.270	
S-Br'	3.587	

ORTEP of 1,3-Dimethylimidazolium-2-Thiocyano Bromide



CHAPTER V

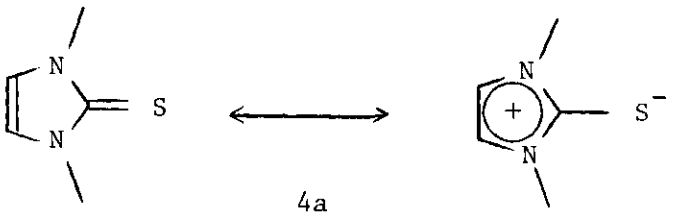
DISCUSSION OF RESULTS

One of the purposes of this research was to develop a synthetic route to highly perturbed thione S-methylides and to examine their chemistry and structure. The synthesis and characterization of a new class of carbonium ion stabilized sulfurances was also achieved.

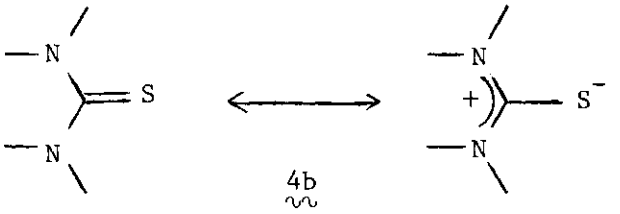
As discussed in Chapter I the stability of perturbed thione S-methylides should be dependent upon the ability of the carbon substituents to stabilize a high degree of charge separation. In order to accomplish such substitution tetra-alkylthiouronium salts were chosen as key intermediates. Two thiones were used as precursors in this work.

1,1,3,3-Tetramethyl-2-thiourea, 4b, is a commerically available thioketone which undergoes ready S-alkylation to form thiouronium salts. The ability of the dimethylamino groups to stabilize an adjacent carbonium ion should be sufficient to effect overall lower energy by perturbation of the molecular orbitals of the ultimate thione S-methylide system. The second thione chosen for this work was 1,3-dimethylimidazole-2-thione, 4a. The imidazole thione was not commercially available and its synthesis was derived from a modification of a procedure which was reported by workers who examined the x-ray crystal structure of this thione.[24] The imidazole moiety provides one of the best centers for incorporation of a carbonium ion since in the 2-position there are not only adjacent nitrogen lone pairs, but in addition the ring system

becomes aromatic upon electron donation to an attached 2-substituent.



4a

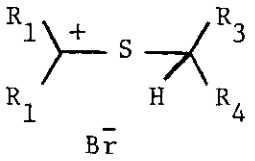


4b

The choice of suitable alkylating agents for the thiones was based on the need for electron withdrawing ability of the final ylide substituent groups. It was, of course, necessary to maintain a single proton on the α-carbon of the penultimate salt which was to be removed in the key deprotonation step to generate the ylide. The following alkylating agents were chosen: bromomalononitrile, methyl α-bromo-α-cyanoacetate, diethyl bromomalonate, ethyl α-bromo-α-phenylacetate, 9-bromofluorene and 9-bromoanthrone. Successful alkylations were achieved in excellent yields for all the above reagents except bromomalononitrile which failed to give any isolable thiouronium salts. The salts which were successfully formed by alkylation of the thiones are listed in Table 8 along with the yields.

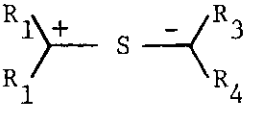
Table 8. List Of Yields Of Salts 6a-b,u-z And Ylides 7a-b,u-z

Salt	Isolated Yield, %	Ylide	Isolated Yield, %
6a,u	97	7a,u	not isolated
6a,v	--	7a,v	--
6a,w	98	7a,w	not isolated
6a,x	--	7a,x	96
6a,y	95	7a,y	87
6a,z	100	7a,z	87
6b,u	--	7b,u	--
6b,v	97	7b,v	not isolated
6b,w	95	7b,w	not isolated
6b,x	--	7b,x	82
6b,y	94	7b,y	89
6b,z	90	7b,z	58

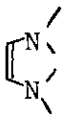


Br^-

6a-b,u-z



7a-b,u-z

a, R_1,R_2 = 

b, $R_1 = R_2 = (CH_3)_2N-$

u, $R_3 = \phi-$, $R_4 = CO_2Et$

v, R_3,R_4 = Anthronyl

w, R_3,R_4 = Fluorenyl

x, $R_3=R_4= -C\equiv N$

y, $R_3= -C\equiv N$, $R_4=CO_2Me$

z, $R_3=R_4= CO_2Et$

The base catalyzed deprotonation of the thiouronium salts proceeded smoothly in all cases and four of the thione S-methylides could be isolated at room temperature. In addition the two dicyano-ylides, 7a,x and 7b,x, were prepared by the method of W. J. Middleton and coworkers.[10] All of the isolable thione S-methylides which were synthesized are listed in Table 8 along with the corresponding yields.

Ylides, 7a-b,x-z, were all characterized by their absorption in the ir ($CHCl_3$) at 1650-1700 cm^{-1} (C=O) and/or 2120-2140 cm^{-1} (C≡N) and consistent proton and carbon-13 spectra. The osmotic molecular weights of these ylides showed them to be monomeric. The proton nmr's of the N-methyl groups and imidazole ring protons as well as the carbanion C-13 shifts indicated the presence of substantial charge spearation across the C-S-C ylide linkage. Table 9 lists selected nmr shifts of ylides 7a,x-z and two reference compounds, the imidazole thione, 4a, and the S-methyl iodide of imidazole thione, 17. This charge separation suggested that the substituent perturbation on the C-S-C system was strong as had been expected.

The synthesis of a variety of perturbed thione S-methylides achieved, attention was turned to the electronic structure of the perturbed systems.

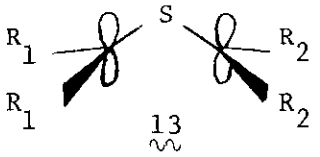
Using an energy-geometry optimized SCF-MINDO/3 procedure*,[33] the

*The bicentric parameters, β_{xy} and α_{xy}, required to modify the core repulsion and resonance integrals for X=N,O and Y=S for this calculation were obtained using only one point; the $\Delta Hf°$ and bond lengths of SO_2 and NS. Since these atoms are not directly united in 13b, error in the calculated relative energies are small. The calculated values for β_{xy} and α_{xy} are: (SO) .422890, 2.077240; (SN) .313170, 1.878176.

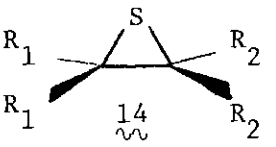
energy surface for closure to the thiirane of the model system 13b was calculated.

Table 9. NMR Chemical Shifts In 7a,x-z Relative to TMS

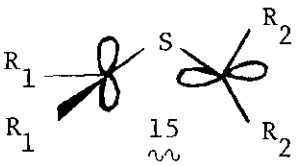
Compound	Chemical Shifts (δ)		
	N-$\underline{CH}_3$	ring $\underline{H}$	C_b^{13}
4a	3.60	6.68	-
7a,x	3.80	7.82	9.9
7a,y	3.93	7.68	34.5
7a,z	4.10	7.00	59.1
17	3.97	7.98	17.7



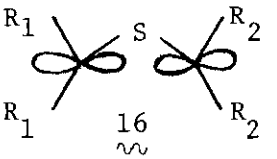
13



14



15



16

a, R_1, R_2 = H

b, R_1 = $N(Me)_2$, R_2 = CHO

The energies of the various π-orbital topologies are shown in Figure 1. In each calculation the orbital orientation was fixed and the C-S-C angle was determined at the total energy minimum. The bond lengths were obtained from the x-ray structure of 7a,z. The allyl anion topology, 13b, was at an energy minimum with a heat of formation of -31.07 kcal/mole when the CSC angle was 137.3°. When the carbanion p-orbital was forced to lie in the CSC plane the heat of formation minimized at -44.28 kcal/mole when the CSC angle was 126.3°. Configuration interaction with the first doubly excited state for this topology lowered the heat of formation by 1.85 kcal/mole and opened the CSC angle to 127.6°. If both the carbonium ion and carbanion p-orbitals were forced to lie in the CSC plane the heat of formation was -42.88 kcal/mole when the CSC angle was 123.3°. Again configuration interaction lowered the heat of formation for this conformation while opening the CSC angle. With this same orbital topology a CSC angle of 104.26° (which was observed in the structure of 7a,z) was imposed and the resulting calculated heat of formation was -38.62 kcal/mole. In another calculation the carbanion p-orbital was forced to assume a 15° inclination to the CSC plane and the CSC angle was maintained at 104.26°. During the course of this calculation the angle of inclination of the carbonium ion p-orbital with the CSC plane was allowed to vary to minimize the heat of formation. At the end of the calculation the heat of formation had minimized at -38.01 kcal/mole with a carbonium ion p-orbital inclination of 16° with respect to the CSC plane. Interestingly, the orbital inclinations from this calculation were conrotatory as would have been predicted from an

application of Woodward-Hoffmann Rules to allyl anion model of the thione S-methylide. In one final calculation a CSC angle of 50° was imposed on the system and both the carbonium ion and carbanion p-orbitals were forced to lie in the CSC plane. The dihedral and valence angles of all four substituents were allowed to vary and the resulting minimum heat of formation, -40.24 kcal/mole, was taken as the value for the thiirane, 14b.

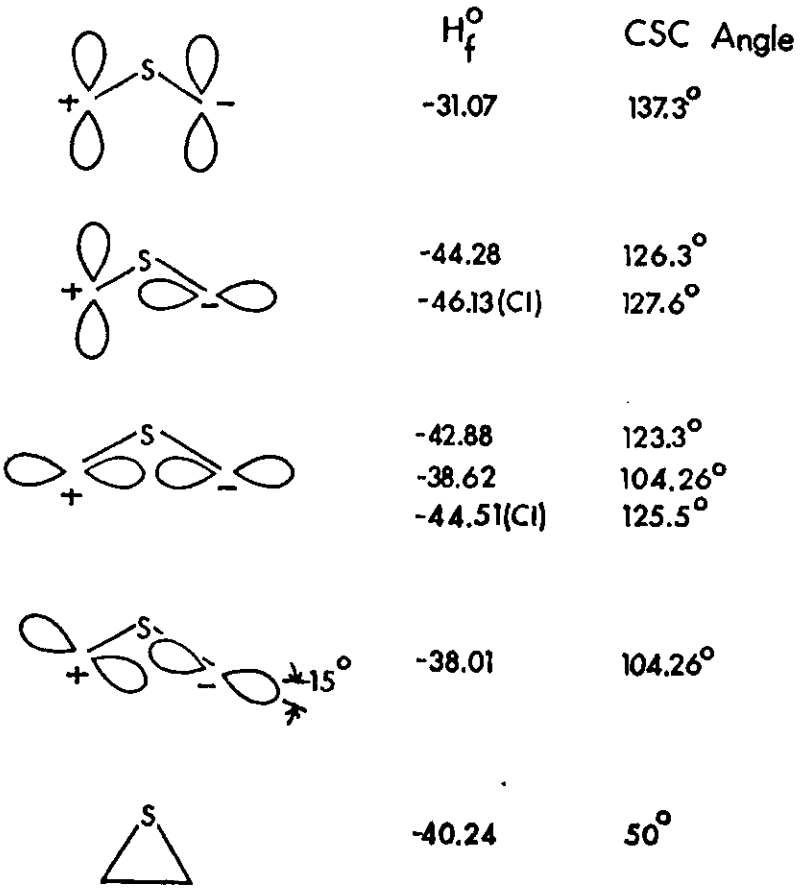


Figure 1. MINDO/3 Heats Of Formation For Various Orbital Topologies In 13b.

After several intermediate points were calculated the potential surface for the conversion of a perturbed thione S-methylide to the thiirane was drawn. The results (Figure 2) reveal a striking departure from the unperturbed system with both end-point structures of higher energy than a non-planar intermediate, 15b. The local surface in the vicinity of 15b was reasonably flat with rotamers such as 16b lying only 1.4 kcal/mole above 15b (recall that configuration interaction with the first doubly excited state lowered but failed to reorder these energies).

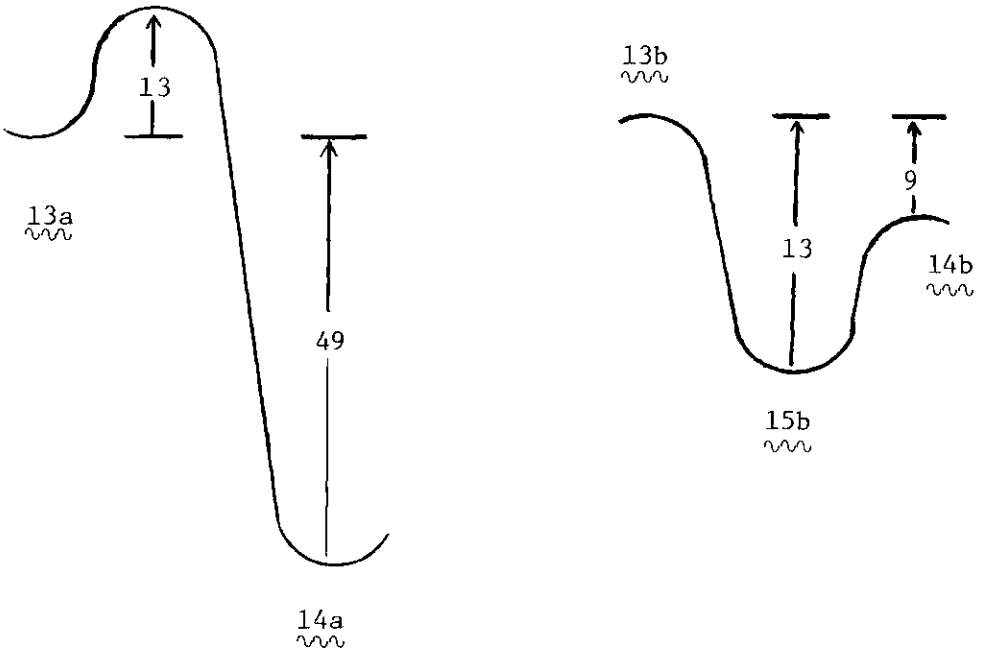


Figure 2. Potential Surfaces For The Conversion Of Unperturbed (Right) and Perturbed (Left) Thione Methylides To Thiiranes. The Energy Differences Are Shown in kcal/mole.

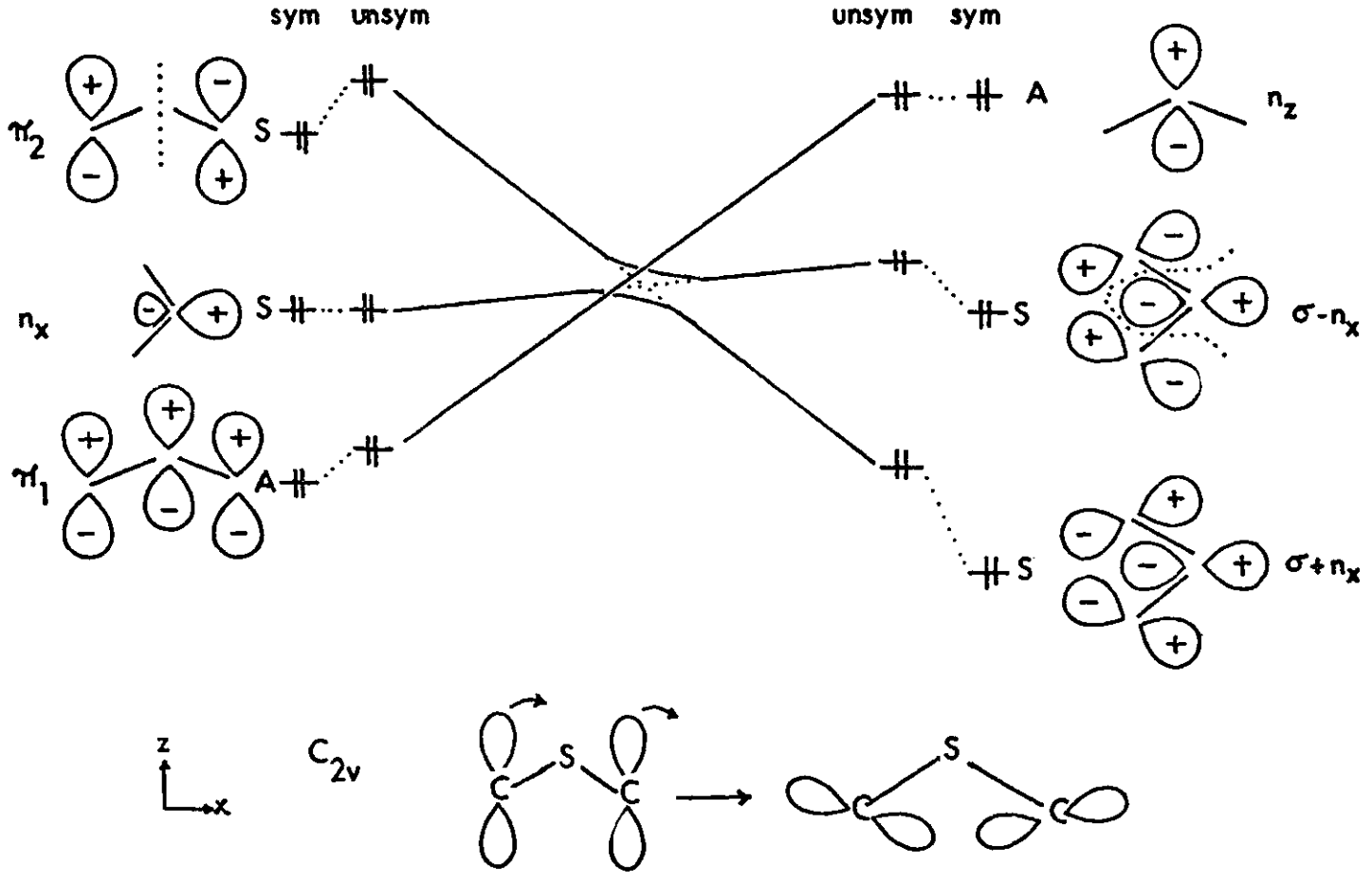


Figure 3. Correlation Diagram For The Pericyclic Conrotatory Closure of 13b to 14b.

The critical molecular orbital whose energy contributes most to reordering the total calculated energy of the planar ylides, 13a and 13b, relative to their respective nonplanar conrotated transition state or intermediate structures is the highest occupied molecular orbital, π_2. The substituent perturbation on this orbital shifts the node toward the π-acceptor substituted carbon thus increasing the electron density on sulfur and raising in π_2 the antibonding character relative to the symmetric structure. The small total energy separation of 15 and 16 is derived from the difference that the π-donor substituted carbon pπ-orbital experiences upon interaction with either the in or out-of-plane sulfur lone pair orbital. The MO correlation diagrams for a conrotatory (C_{2v} symmetry) ylide to thiirane closure is shown in Figure 3.

With the above theoretical analysis in mind the x-ray structure of 7a,z provides most striking results.

The C_aSC_b angle found is an unexceptional 104.26° while both the C_aS and C_bS bond lengths are 1.7Å and thus intermediate between a CS double and single bond similar to that observed for 1,2-sulfonium methylides.[35] However, the most extraordinary structural feature is the inclination of the C_a and C_b substituent planes to the C_aSC_b plane which results in a carbon pπ-orbital topology as shown in Figure 5. The remarkably close correspondence to the theoretically derived structures 15-16 is notable.

Some conclusions as to the role of a central second row atom in conjugative interaction between the carbon termini in 1,3-dipolar ylides may be drawn from magnetic resonance spectroscopy studies. The efficiency of charge transmission across the methylide sulfur atom is evident

from the effect of various combinations of electrons withdrawing substituents at C_b on selected C^{13} and H^1 nmr chemical shifts in the system 7a,x-z (Table 10).

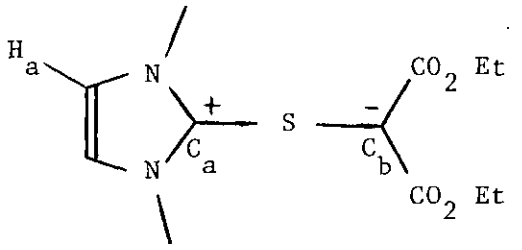


Figure 4. Reference Positions In 7a,z.

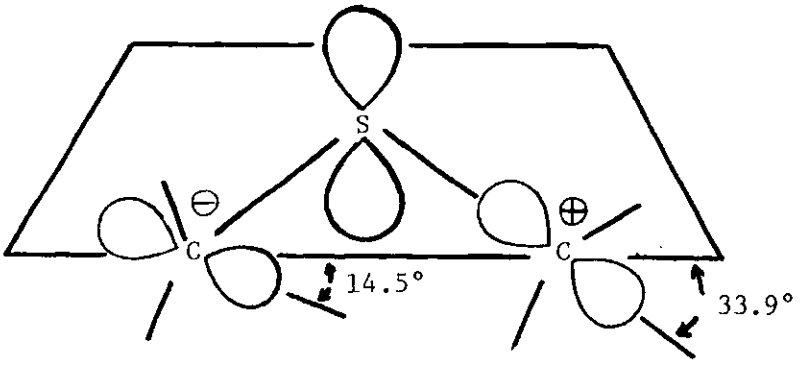


Figure 5. π-Orbital Topology of 7a,z.

Table 10. NMR Chemical Shifts In 7 Relative To TMS In DMSO-d_6

Compound	Chemical Shift (δ) H_a	C_a	C_b
7a,x	7.81	144.2	9.9
7a,y	7.69	144.1	34.5
7a,z	7.51	146.1	59.1

A correlation appears to exist between the ring current induced diamagnetic anisotropic deshielding of H_a with the degree of total shielding of C_b while the relative shifts of C_a remain small and consistent with the view that ring current variations have little effect on C^{13} shifts.[36] To further identify the mode (σ vs π) of charge transmission in perturbed thione methylides the C_a^{13} shift of 7b,z was compared with some reference compounds, 4b and 18 (Table 11).

$(Me_2N)_2\overset{+}{C}_a\overset{-}{S}C(CO_2Et)_2$ $(Me_2N)_2C_a{=}S$ $(Me_2N)_2\overset{+}{C}_aSMe\ I^-$

7b,z 4b 18

The calculated values shown in Table 11 were based upon the following assumptions, (a) the dominant contribution to the differences in chemical shift were nearest neighbor dependent and derived from variations in

Table 11. Observed C_a^{13} Chemical Shifts (Relative To TMS) And Calculated Parameters

Compounds	δ(obs)	$\sigma^{(2)}_{xyz}$	$\sigma^{(2)}_{z}$	P_{ii}	$\Sigma_j P_{ij}$	$P_{ij}S_{ij}$
4b	-193.9	-190.9	-185.4	.6822	1.4542	.1446
7b,z	-180.8	-182.5	-177.3	.7509	1.1554	.1076
18	-174.5	-175.6	0170.7	.6811	1.4294	.0684

the second-order paramagnetic shielding tensor, $\sigma^{(2)}_{xyz}$, for the 2p orbitals of C_a, (b) the mean excitation energy, ΔE, was localized at C_a-S and could be approximated by the calculated $n_s \rightarrow \pi^*$ transition,[37] and (c) the largest variation in the rotationally averaged second-order term arose essentially from $\sigma^{(2)}_z$ of the carbon p_π-orbital. Using the Karplus-Pople relationship,[38] $\sigma^{(2)}_z \simeq [-e^2h^2/48m^2c^2a_o^3]\,[3.25 - .35\,(P_{ii}-1]^3\,P_{ii} + \Sigma_j P_{ij})/\Delta E]$, and the diagonal ($P_{ii}$) and off-diagonal ($P_{ij}$) density matrix elements as well as ΔE from a SCF-CNDO2 calculation for C_a in 13b, 4b, and 18; the calculated values were fitted to a line $\sigma^{(2)}_{xyz} = 1.0383\,\sigma^{(2)}_z - 1.6$ ppm. A planar geometry was assumed for 18, but 13b was allowed to adopt the three-dimensional structure found for 7a,z. With inclusion of sulfur d-orbitals in the basis the order of calculated C^{13} shifts is the same as the observed values, no correspondence between the C_a orbital electron population (P_{ii}) or the bond orders (P_{ij}) and this observable are apparent. However, the C-S bond order when scaled by the overlaps (S_{ij}) to represent its contribution to the total

Mulliken population[40] does correlate with the observed shifts. Although such a population analysis is at best approximative it does seem to qualitatively indicate a CS partial double bond providing the stabilizing conjungative link between the two charged centers through sulfur. The inclusion of higher-order d-orbitals of proper symmetry in the sulfur basis for the orbital description no doubt leads to more favorable charge distribution (increased electron density at the electropositive sulfur) due primarily to modification of the non-bonding π-orbitals. The bonding contribution of d-orbitals to the actual total energy of such sulfur compounds is controversial. The net lowering of the calculated SCF energy with a d-orbital inclusive basis may not be due to a net decrease in the occupied orbital energies but a result of altered couloumb and exchange terms.[41]

The results of the molecular orbital calculations on the highly perturbed thione S-methylide systems suggest that decomposition products arising from closure to the thiirance would be precluded if other decomposition modes were possible since the thiirane lies high in energy.

To examine what decomposition modes are likely to occur in the absence of thiirane intermediates it is useful to inspect HOMO and LUMO representations of the highly perturbed ylide systems. Figure 6 gives a graphical representation of the frontier orbitals in the model system, 16b, as determined by an SCF-CNDO2 calculation.

The HOMO is primarily the carbanion P_x orbital while the LUMO has a greater sulfur contribution than the carbocation P_y. Intermolecular HOMO-LUMO interaction would therefore suggest an initial CS union to form

the sulfurane 19. Formation of a second CS bond would carry 19 to 20 which could undergo a chelotropic loss of a thione to give 21 which in turn would also undergo chelotropic fragmentation to give an alkene and a second thione molecule. The possibility also exists that 19 could undergo an internal displacement reaction to liberate a thione and form 21 directly. However, the deviation from linearity at the displacement site would be substantial and would perhaps eliminate this reaction path. Thus, decomposition of the highly perturbed ylides to alkenes and thiones would be expected from a theoretical frontier orbital approach. The experimental evidence supports this conclusion.

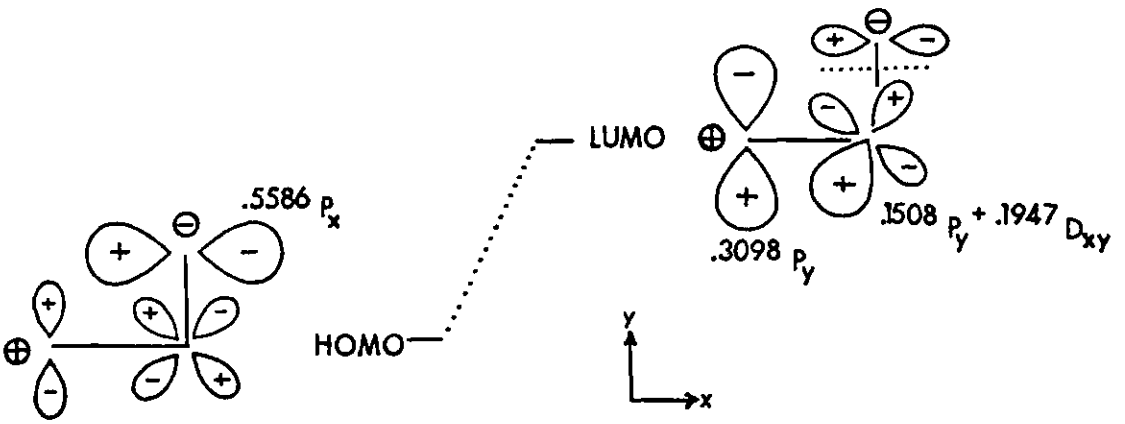
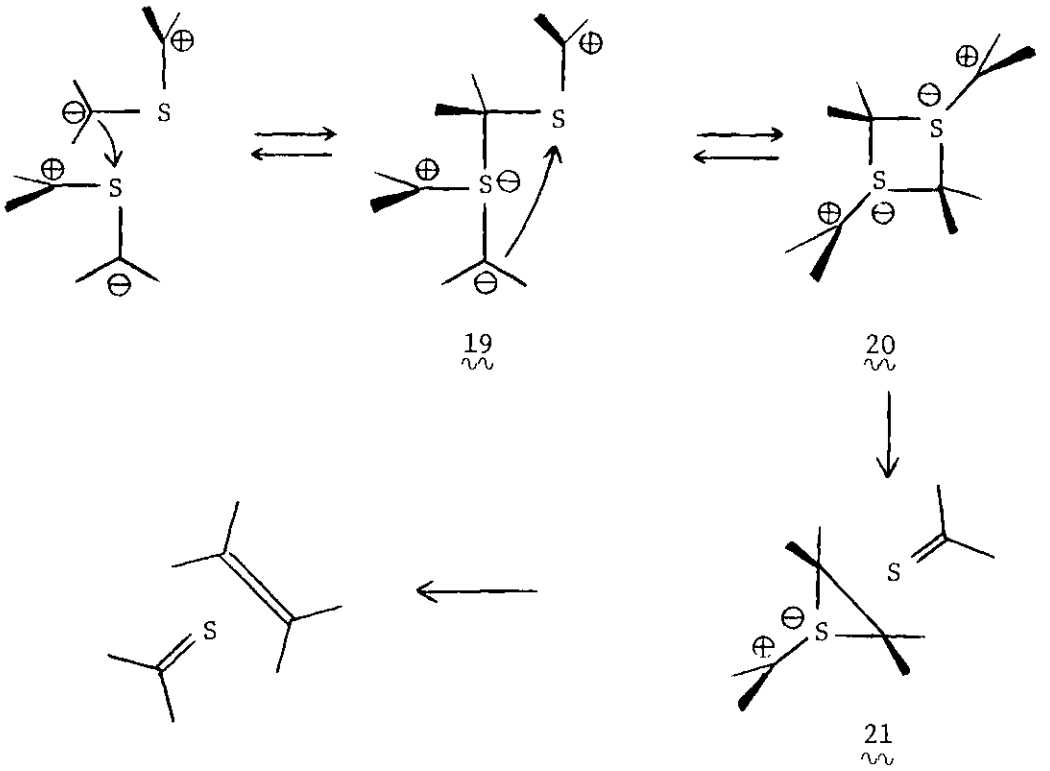


Figure 6. Representation of the HOMO and LUMO of 16b with Calculated Coefficients. The Energy Separation is ∿ 11 ev.

All of the perturbed ylides synthesize in this work decomposed upon heating to an alkene and a thione and in each case both products could be isolated. It is also worthy of note that no carbenes could be

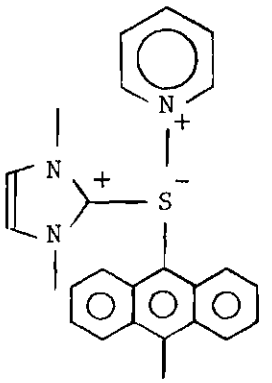
detected by the addition of trapping reagents in any of the decomposition reactions (this would have been suspected since simple sulfonium ylides do decompose by carbene intermediates[42]). While alkenes and thiones were major products from the decomposition reactions, they were not the sole products. The thermal decompositions result in complex mixtures containing many different products but the thione and alkenes were the only products present in large enough amounts to be cleanly detected and isolated.



19 20 21

The varying stabilities of the perturbed thione S-methylides can be rationalized in terms of a frontier orbital approach. The

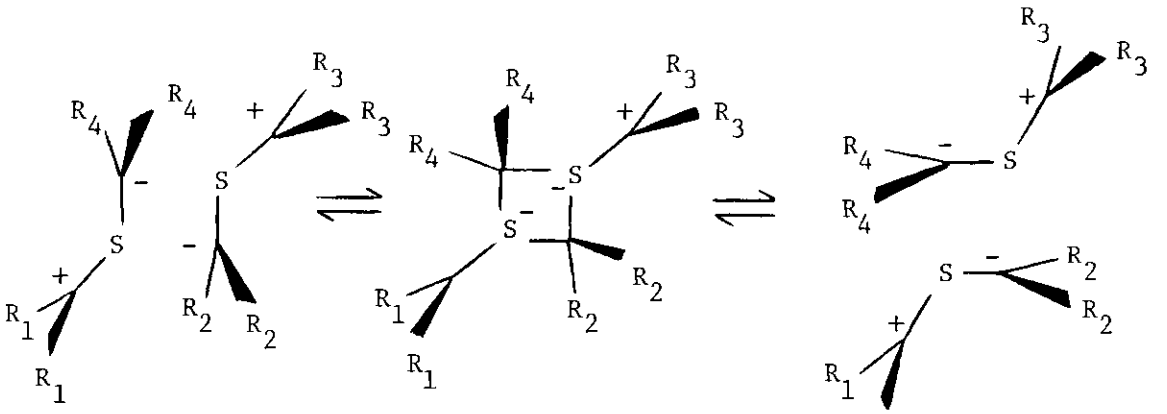
dicarboethoxy ylides, which were by far the most stable ylides, derive this property by a favorable change in the nodal properties of the π-system. As the electron withdrawing ability of the carbanion substituents decreases, nodes in the π-system shift back toward the donor substituents which in turn gives rise to a decrease in sulfur contribution to the LUMO. Thus the initial CS bond formation necessary to give 19 is a less favorable process and the decomposition will require a higher activation energy. This is to be contrasted with the anthronyl and fluorenyl ylides where more symmetrical nodal properties with respect to sulfur also occurs but this effect is more than compensated by vastly increased electron density at the anion carbon due to a loss of electron withdrawing ability of the substituents (note that the donating ability of the donor substituents is constant) and results in increased overlap of the carbanion orbital with the sulfur LUMO and thus rapid intermolecular CS bond formation. There should be a range of electron withdrawing substituents which gives rise to the best balance between nodal positions in the LUMO and HOMO and the electron density at the carbanion center. In the systems studied the optimal balance and greater stability was achieved with two carboethoxy electron acceptors while increased (dicyano) or decreased (fluorenyl) electron accepting ability produced less stable ylides. The lifetime in solution of the anthronyl ylides could be increased by blocking the LUMO with pyridine and the formation of intermediates with 22 would explain why the color of the anthronyl ylides was more persistent in the presence of pyridine.



22

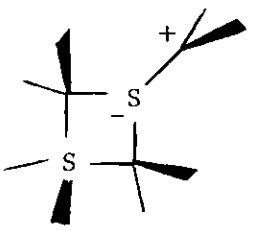
An interesting ylide exchange was also observed in these highly perturbed thione S-methylides. Upon admixture in methylene chloride solution at 27° a pair of thione S-methylides which are differentiated by nonidentical sets of π-donor and acceptor substituents undergo rapid ($t_{1/2}$ < 5 minutes) exchange of the latter substituent. For example, 7a,x reacts with 7b,z to afford 7a,z and 7b,x furthermore the direction of this particular exchange is enforced by the ready decomposition of 7b,x to 4b and TCNE. Similar ligand exchange reactions have been reported for sulfonium methylides and a degenerate ligand exchange mechanism has been suggested to account for the facile racemization of chiral sulfur in certain of these ylides.[43] The mechanism of substituent stabilized thione S-methylide multiple ligand exchange may be rationalized by a sequence analogous to the decomposition reactions. Again CS union through HOMO-LUMO interaction would bring about the formation of 19 and ultimately 20. The bis-sulfurane 20 has two possible modes of cleavage

to give ylides. It may reopen breaking the bonds that were created during its formation, which would return the starting ylides, or it could fragment by alternative S-C bond clevage to give two new ylides.



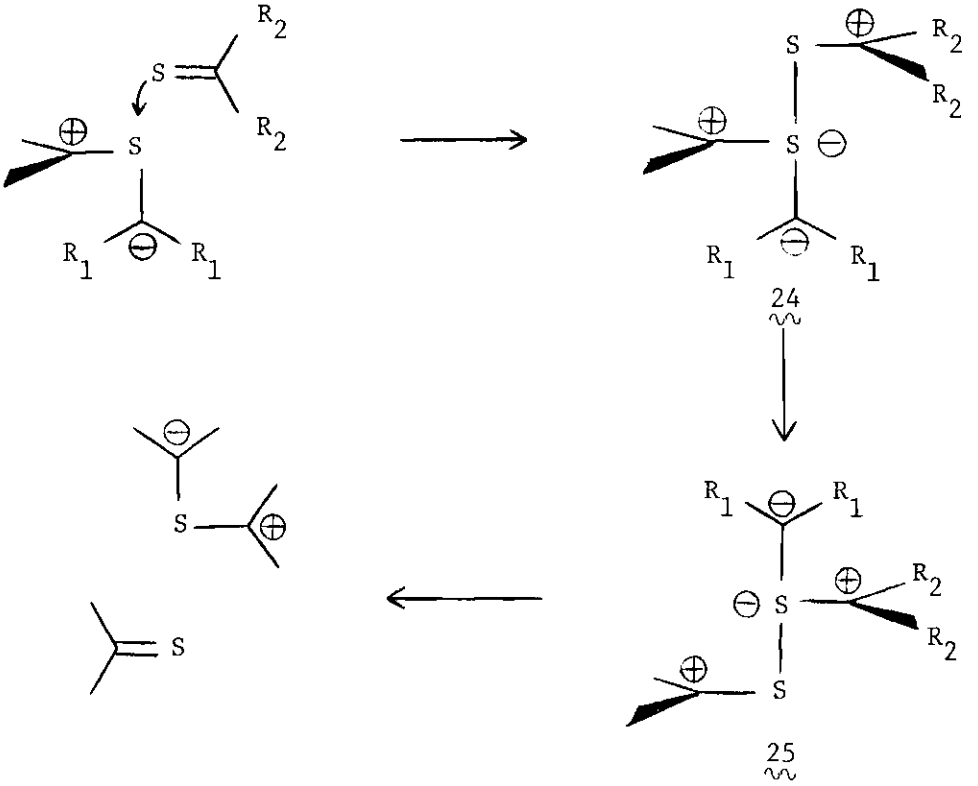
20

With sulfonium ylides an extremely slow exchange of methylide groups was observed and this exchange can be viewed as involving the reluctant formation of intermediates like 23 which could fragment in a manner analogous to 20.



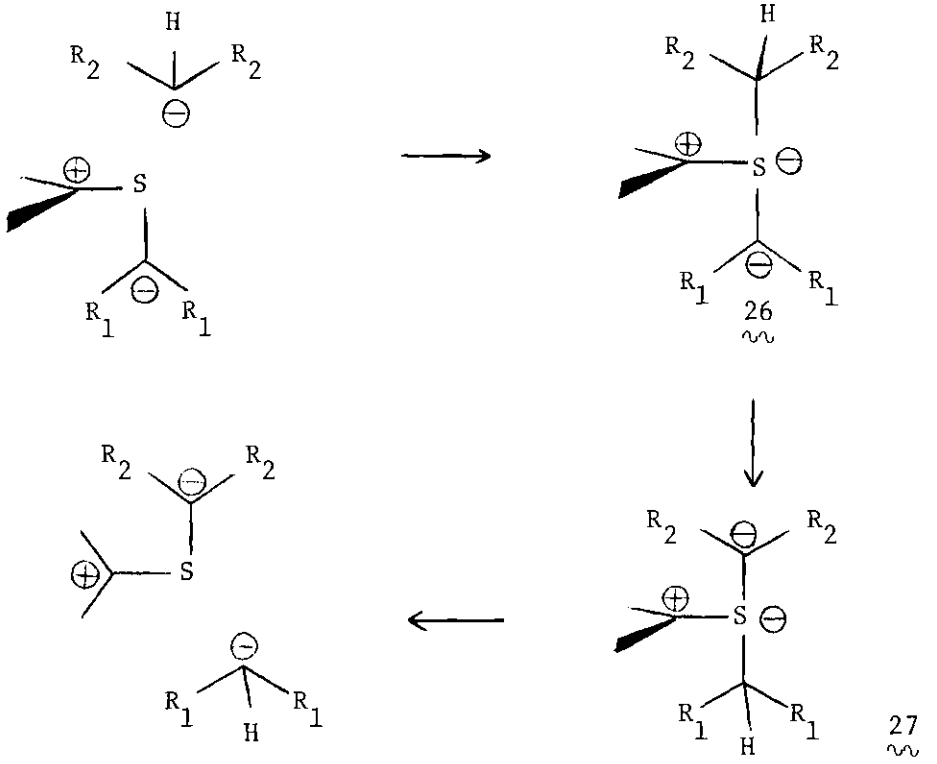
23

The thione S-methylides derived from 1,3-dimethylimidazole-2-thione as a precursor undergo a facile reaction with tetramethylthiourea in methylene chloride solution to afford the tetramethylthiourea S-methylides and imidazolethione (4a). This process which is equivalent to ligand transfer between ylide and thione, appears to proceed in a direction to provide the ylide with the less effective π-electron donor substitutents. Rationalizing this behavior in a manner consistent with the other multiple ligand exchange and decomposition reactions requires an intermediate 24 in which the equivalent of a 1,3-shift of the π-electron withdrawing groups occurs to give 25, the driving force for the shift is dictated by the formation of the most stable sulfurane as determined by the electron withdrawing ability of the equatorial substituent.

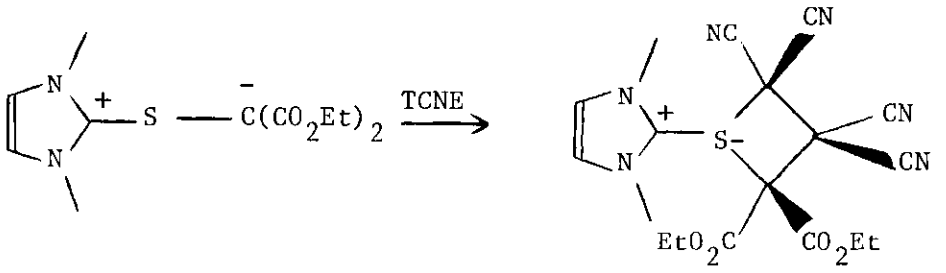


Although no exchanges could be observed between sulfonium ylides and thiones or between dialkylsulfides and thione S-methylides, a recent article[44] reports on a tetramethylthiourea catalyzed decomposition of selenonium ylides. This catalytic reaction reported may involve the formation of thione S-methylides which undergo a rapid decomposition to alkenes and regenerate tetramethylthiourea.

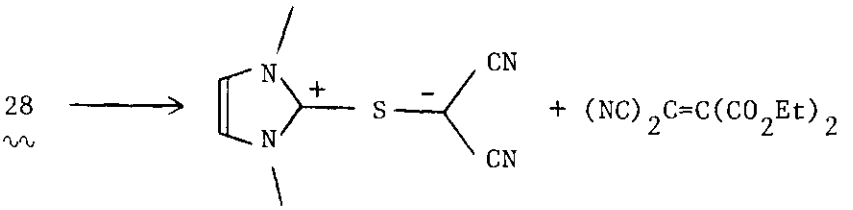
The substituent perturbed thione S-methylides undergo another reaction which is related to the ligand exchanges. Malononitrile and the diester ylide 7a,z undergo a reaction in methylene chloride at 27° to give the dicyano ylide 7a,x. Again, this reaction can be visualized as a ligand displacment proceeding through the intermediate hypervalent sulfuranes 26 and 27.



One final reaction observed for the perturbed thione S-methylide 7a,z was the reaction with TCNE to form the dicyano ylide 7a,x. This reaction might proceed through the intermediate 28 to give the observed products.



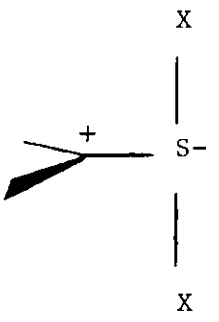
28



The reactions and decompositions of the substituent perturbed thione S-methylides have one common proposed mechanistic feature, the formation of a hypervalent sulfur intermediate. The ability of sulfur to accommodate excess electron density in such sulfuranes is aided by the presence of an equatorial π-acceptor. For the hypervalent intermediates involved in the reactions of the substituent perturbed thione S-methylides the equatorial acceptor orbital was provided by the stabilized carbonium ion present at the carbon bearing the donor substituents. An extension of the idea of carbonium ion stabilized

sulfuranes is seen in the dibromothione.

The tricoordinate tricovalent sulfuranes like 8a derive their stability in a manner very different from the more conventional tetracoordinate tetracovalent sulfuranes examined by Martin and coworkers.[16,17]



8a

The bonding scheme in the sulfurane hypervalent system can be simply depicted in terms of the schematic representation in Figure 7.

The lowest lying σ_z orbital is one which bonds both apical substituents to the central sulfur and involves the delocalization of a single electron pair over a 3-center system. The second orbital, n_z, is normally a non-bonding orbital which places substantial electron density on both of the apical substituents. The increased electron density on these axial positions is the source of the commonly accepted idea that the most electronegative substituent is always found in the apical positions of a trigonal bipyramidal species. The highest lying orbital,

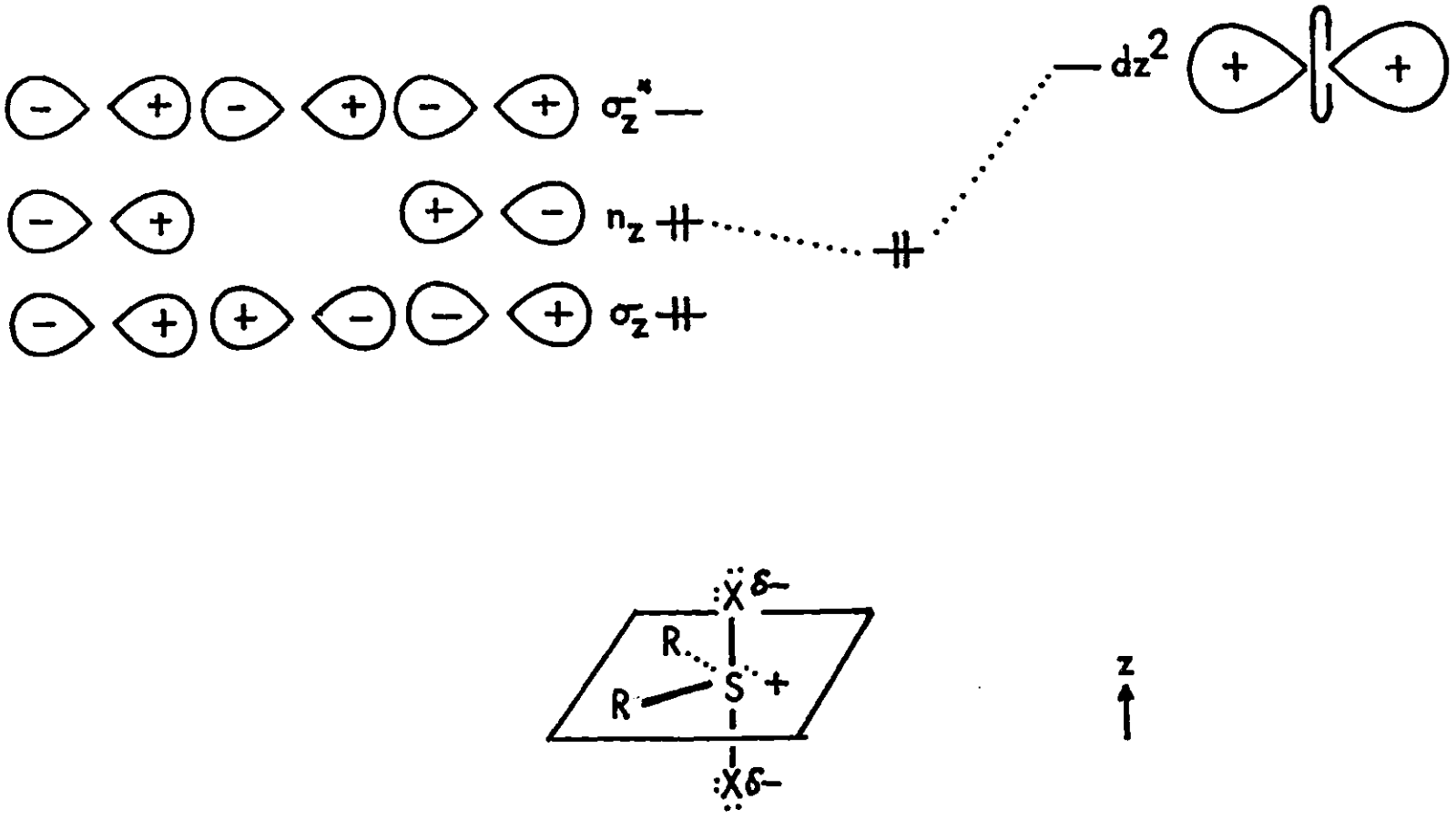
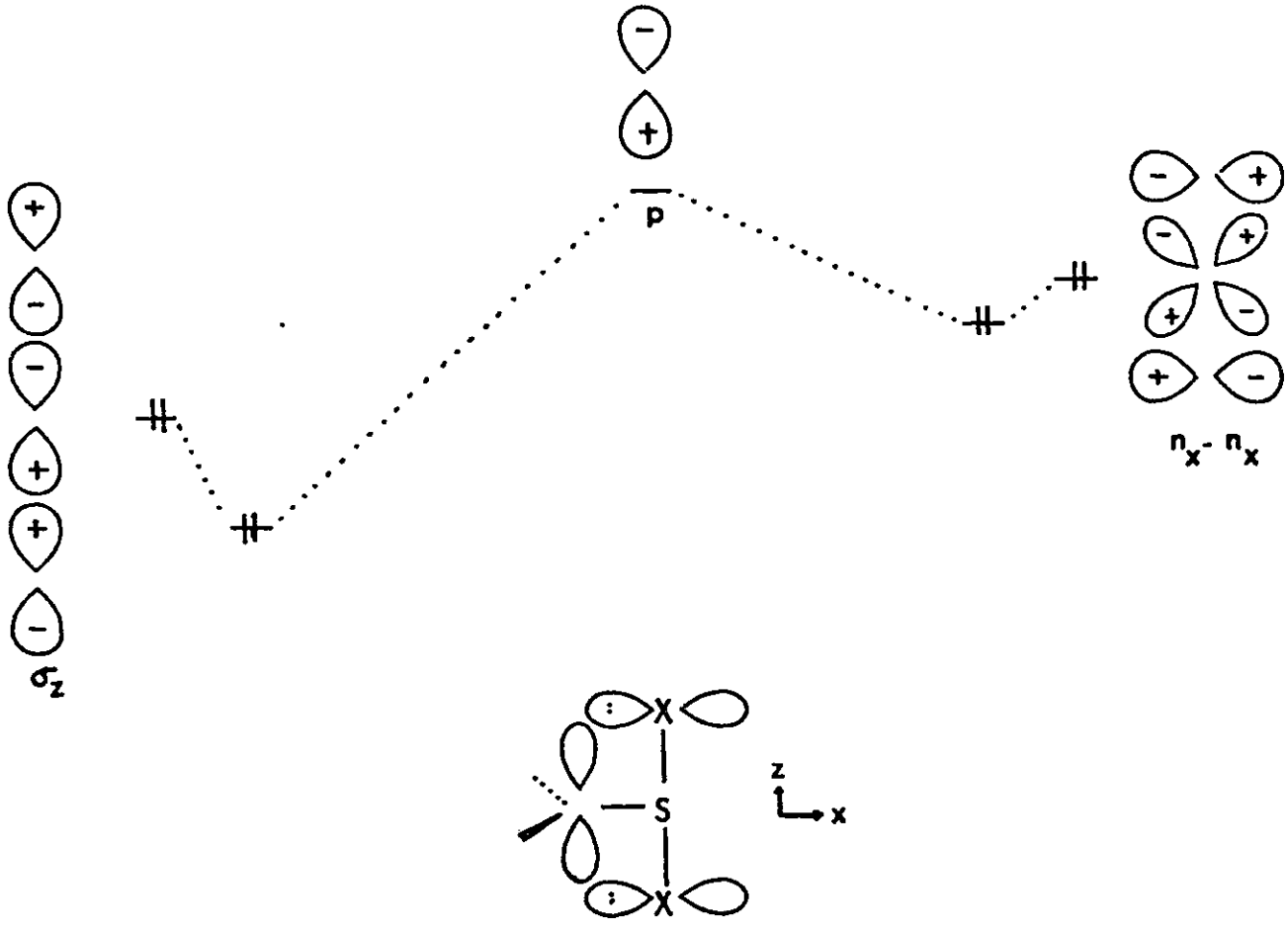


Figure 7. Molecular Orbital Representation In Linear 3-Center Hypervalent Systems.

σ_z^*, is one in which both the apical ligands are antibonded to the central sulfur, fortunately this orbital is unoccupied in the 3-center, 4-electron bonding systems. The system can gain additional stabilization by mixing central atom higher order orbitals with the MO's depicted in Figure 7. A sulfur dz^2 orbital would be of proper symmetry to interact with the second n_z level. This interaction would not only lower the energy of this level but would also cause increased bonding of the apical substituents to the central sulfur. The interaction of the MO's in Figure 7 with a π-acceptor orbital (e.g., a carbonium ion) would give rise to a stabilization of both the σ_z and σ_z^* levels. This stabilization is represented diagramatically in Figure 8. Note that σ_z is lowered by about 1 ev by this interaction but that there is a second interaction of the acceptor orbital with non-bonding pairs on the apical substituents that gives an additional 0.2 ev of stabilization, thus, the total calculated stabilization for this orbital topology would be 1.2 ev. However, this arrangement is not the only reasonable topology for the tricoordinate tricovalent sulfuranes like 8a.

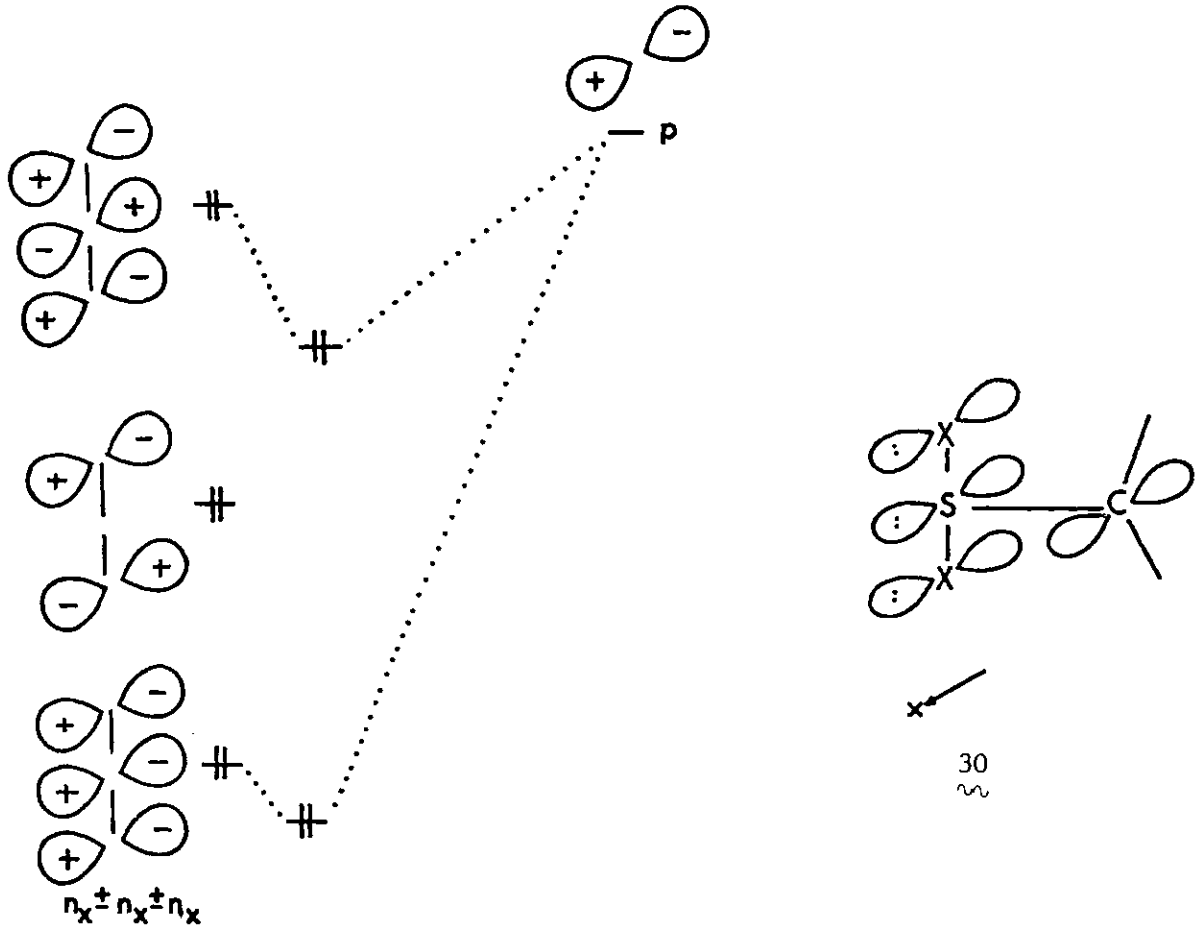
If the π-acceptor orbital is rotated by 90° a new set of interactions with the non-bonding pairs on sulfur and the two ligands arise. These resultant levels are shown in Figure 9. At the left in Figure 9, the three possible combinations of lone pair interactions are shown. The highest and lowest of these levels are of a symmetry which can interact with the acceptor orbital. The total stabilization for this orbital topology would be 3.21 ev.

On a solely electronic basis the completely planar form, 30, of the dihalothiones would be preferred over the perpendicular form, 29.



29

Figure 8. Diagrammatic Representation Of The σ_z Level Interactions With An Equatorial π-Acceptor.



30

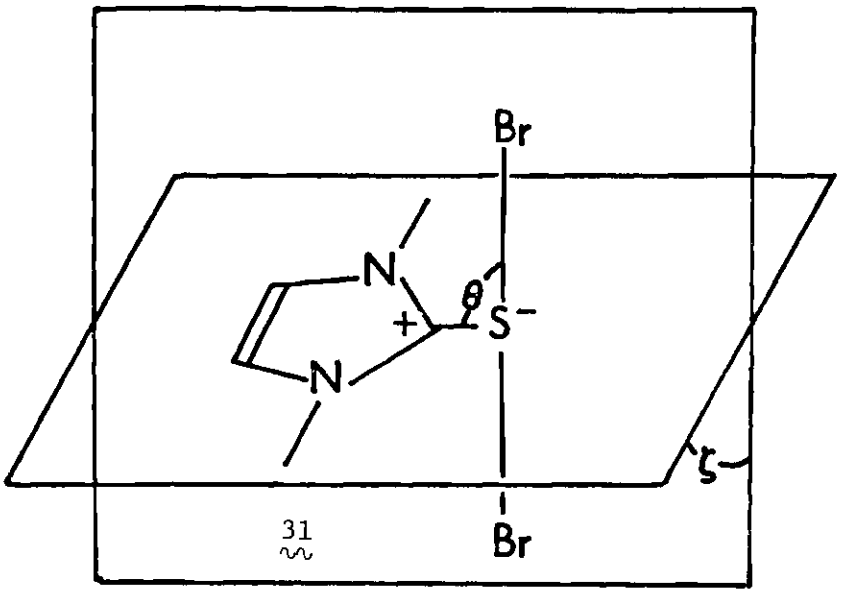
Figure 9. Diagrammatic Representation of the Interactions Of Non-Bonding Pairs With An Equatorial π-Acceptor.

However, in the dihaloimidazolethione system one other consideration must be kept in mind; the planar form would necessitate a severe steric interaction between the N-methyl groups on the imidazole ring and the apical ligands. Models show that in the planar form an apical ligand 2.4 Å away from sulfur would approach the N-methyl hydrogens within about 0.7 Å. This most severe steric interaction would be expected to destabilize the planar form, 30, relative to the perpendicular form, 29.

This steric control of the perpendicular geometry would result in the greatest electronic stabilization of the hypervalent bonding system although the total energy would be higher. One final effect of a carbonium ion as a π-acceptor would be a couloumbic lowering of the energy of the entire electron rich hypervalent bonding system (this would also increase higher order orbital participation on the central atom in the bonding schemes).

In the light of the above theoretical argument, it is remarkable to note the close resemblance of the x-ray crystallographically determined structure of the dibromoimidazolethione, 31, to the theoretically derived structure, 29.

In complete agreement with theory, sulfurane 31 has an axial 3-center geometry almost colinear ($\theta = 8.74 \pm .8°$) with elongated bonds of 2.520 and 2.477 $\pm$ .007 Å (cf. 2.3 Å in S_2Br_2). The equatorial CS bond length is 1.730 $\pm$ .02 Å. It should be noted that 31 participates via a non-planar geometry ($\zeta = 90.0°$) in the interaction qualitatively described in Figure 8 due to the steric effect of the N-methyl groups.

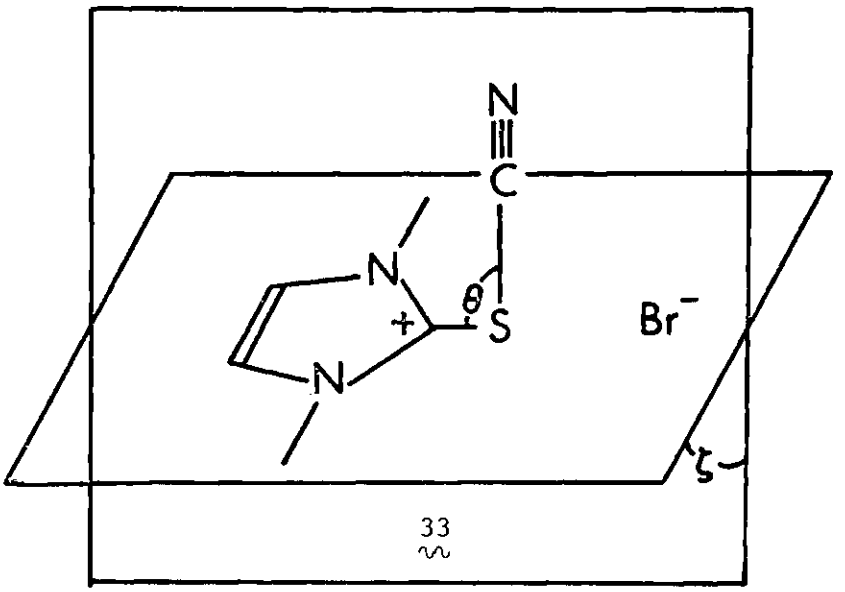


31

$\theta = 87.9°$
$\zeta = 90.0°$

The stability offered the sulfurane structure by the equatorial carbonium ion is indeed phenomenal as the normally weak covalent sulfur-bromine bond is now incorporated into a sulfurane structure in an apical position where bonds are generally longer and weaker than "normal" sigma bonds.[45] The S-iodo-S-bromoimidazole thione (32) structure is even more remarkable in terms of stability.

Attempts to synthesize trivalent sulfuranes containing an axial cyanide were unsuccessful. Cyanogen bromide reacted with the imidazole-thione to form the ionic imidazolium-2-thiocyano bromide, 33.



33

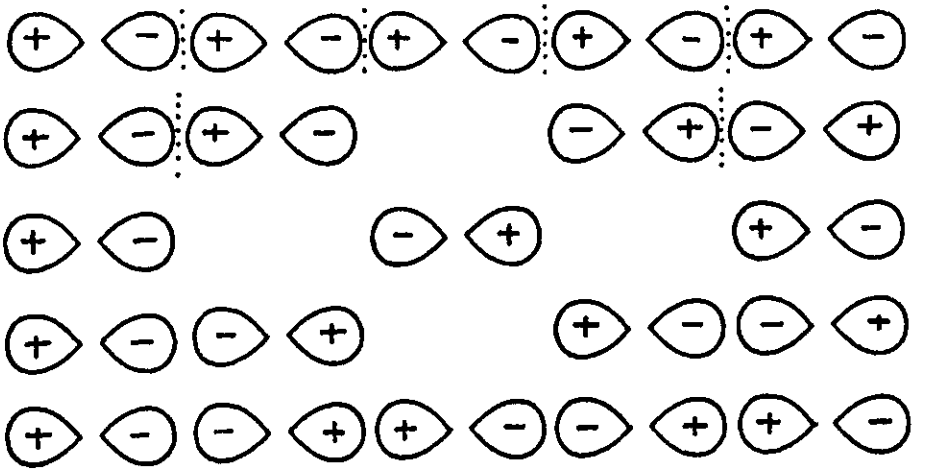
$\theta = 96.2°$

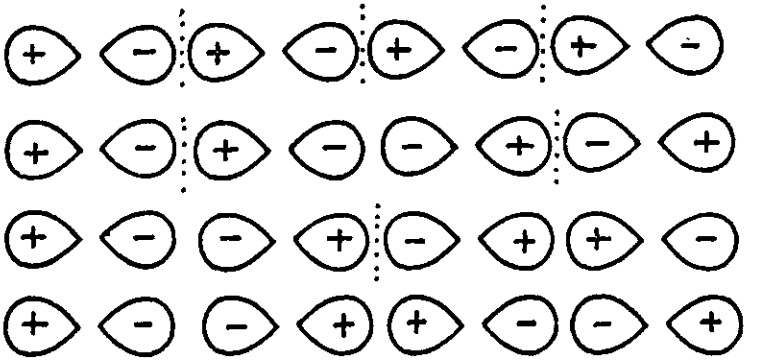
$\zeta = 90.0°$

By x-ray crystallography the covalent attachment of the cyano group is characterized by an axial SC bond length of 1.76 Å orthogonal (θ = 96.2°, ζ = 90.0°) to the ring system while the bromide ion occupies a lattice position 3.27 Å away from the nearest sulfur.

The observed incongruity between the appearance of a hypercovalent or an ionic molecule as a function of ligand structure is clearly independent of ligand electronegativity. If one considers an electron-rich multicenter bond with the hypervalent center participating by predominantly p-orbital bonding, two general patterns of occupied, symmetry-adapted, delocalized molecular orbitals appear.

If an even number of atoms participates in a hypervalent system, antibonding orbitals arise and are filled immediately after the occupancy





Atomic Orbitals	Electrons	Molecular Orbitals
2n+3	4n+4	2n + 1 nonbonding
2n+4	4n+6	2n + 2 antibonding

Figure 10. Representation Of Even And Odd Membered Linear Hypervalent Systems.

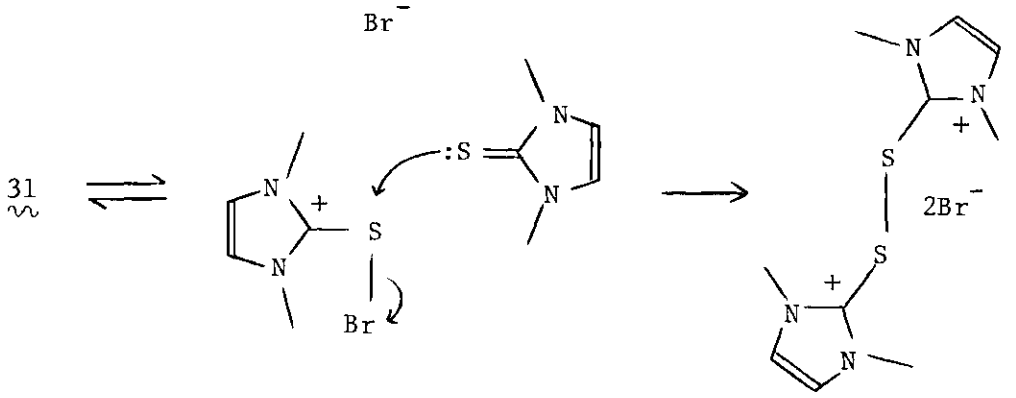
of the lowest molecular orbital. Thus, these even membered hypervalent systems have strong destabilizing antibonding filled levels.

In systems where an odd number of atoms participates in a hypervalent system, only non-bonding molecular orbitals appear at levels which need be occupied and thus these systems experience no antibonding electronic interactions.

In more general terms, for 2n+3 (n = 0,1,2, ...) atomic orbitals combined to give molecular orbitals for 4n+4 electrons there are 2n+1 occupied non-bonding levels which do not contribute to vicinal bonding in the array and for isolable hypervalent molecules requires electronegative ligands to stabilize the resultant electron density as is observed for 31. Conversely, 2n+4 atomic orbitals combined to give molecular orbitals for 4n+6 electrons results in 2n+2 occupied anti-bonding levels which are destabilizing regardless of ligand electronegativity, as for example, the hypervalent counterpart of 33.

Since the dibromosulfurane, 31, can be converted to the bis-imidazolium disulfide 34 by the action of the imidazolethione, 4a, it seems logical to conclude that one of the most electrophilic sites in 31 must be at sulfur since only attack of an incoming nucleophilic thione at sulfur would lead to the formation of the disulfide 34.

The failure of 31 to give a sulfine on treatment with aqueous base was due to a prior dissociation to bromine and imidazolethione when 31 is placed in aqueous solutions. This suggests that bromine is an alternate electrophilic site on the half dissociated form of 31.



The dissociation of 31 into bromine and thione was also evidenced by the failure of carbon bases like sodio-diethylmalonate to form thione S-methylides as had been anticipated. Thus, while the S,S dibromide 31 is a extremely interesting molecule from a theoretical point of view it is of little use as an intermediate in ylide synthesis.

CHAPTER VI

CONCLUSIONS

Thione S-methylides have been prepared in two steps from thioureas and alkylating agents. The formation of the intermediate thiouronium salts (6) proceeded smoothly in excellent yields and the base catalyzed deprotonation of these salts was easily accomplished with a suitable base such that thione S-methylides could be expediently prepared under a variety of conditions.

The substituent perturbed thione S-methylides were represented by a theoretically derived model which suggested the highly perturbed ylides should adopt a structure which was intermediate between the allyl anion form and the thiirane. Furthermore, even in these highly perturbed systems the orbital topology represents a conrotatory orbital orientation of the carbon termini.

The chemistry observed for the perturbed thione S-methylides was explained by a central hypervalent species which was derived by the examination of frountier orbitals. Thus the decomposition of the perturbed thione S-methylides results in the formation of alkenes and thiones without carbene intermediates. The transfer of the methylide groups between two non-identical ylides was observed to proceed rapidly at room temperature presumably through hypervalent intermediates like 20. A transfer of methylide groups between ylide and thione was also observed and again presumably proceeding through hypervalent

intermediate like 24 and 25. A few other ligand exchanges on the thione S-methylides were observed and these also most likely proceed through hypervalent intermediates.

The action of halogens on the imidazole thione 4a resulted in the formation of a new class of sulfuranes (8a). The dihalothiones synthesized represent a new class of tricoordinate tricovalent sulfuranes which show an unusually high degree of stability which was demonstrated by the high thermal stabilities of the dibromo (31) and iodobromo (32) sulfuranes.

The development of an even-odd parity rule suggested that only hypervalent systems containing an odd number of atom members in the linear hypervalent system were possible as stable structures.

APPENDIX

Structure Factor Table For 1,3-Dimethylimidazole-2-Thione S-Dicarboethoxymethylide

K	L	FO	FC
	H= -8		
0	10	15	13
	H= -7		
0	4	18	17
0	12	17	15
1	3	20	21
1	8	13	13
1	9	9	7
1	11	8	9
1	12	3	5
1	13	9	9
2	4	14	12
2	5	9	6
2	7	10	11
3	5	9	8
3	6	19	18
3	8	17	19
4	4	13	12
4	5	13	13
4	6	14	13
4	9	12	12
4	12	11	8
5	7	15	15
5	8	9	6
5	9	9	9
5	11	3	4
6	6	9	4
6	8	12	10
6	9	9	8
	H= -6		
0	4	12	15
0	6	21	21
0	10	15	12
0	12	8	10
0	14	11	9
1	5	15	14
1	7	16	13
1	9	16	15
1	10	9	10
1	11	10	10
2	1	9	3
2	5	12	12
2	6	23	22
2	7	18	16
2	8	8	8
2	9	20	20
2	10	20	20
3	4	8	8
3	5	8	7
3	6	13	13
3	8	27	27
3	9	11	12
3	10	32	32
3	11	13	11
4	3	8	7
4	4	10	11
4	6	14	16
4	7	17	17
4	8	17	17
4	9	19	20
4	11	20	21
4	12	12	7
5	1	8	6
5	2	10	3
5	4	13	12
5	6	7	5
5	8	10	11
5	9	8	12
5	10	8	2
5	11	26	25
5	12	16	15
6	2	15	12
6	4	13	13
6	8	11	11
6	10	21	21
7	5	12	9
7	6	15	15
7	7	17	18
7	8	16	15
8	6	10	11
8	7	18	19
8	9	15	17
8	10	14	13
9	7	9	2
	H= -5		
0	2	10	10
0	10	10	5
0	12	17	16
0	14	15	18
1	1	18	17
1	3	13	13
1	4	10	11
1	5	14	7
1	7	24	26
1	9	7	6
1	11	16	14
1	13	19	18
2	1	10	12
2	2	22	22
2	4	8	11
2	5	8	1
2	6	8	9
2	7	10	11
2	8	11	12
2	9	24	25
2	10	14	14
2	12	15	12
2	13	9	7
3	5	14	16
3	6	27	28
3	9	9	11
3	10	24	22
3	12	23	23
4	0	8	7
4	1	8	9
4	4	11	10
4	6	7	7
4	8	24	26
4	9	25	25
4	10	12	11
5	2	9	8
5	3	17	18
5	4	8	8
5	6	8	7
5	7	12	11
5	8	12	12
5	9	9	4
5	11	15	18
5	12	9	9
5	13	24	25
6	3	9	11
6	4	20	21
6	6	11	12
6	8	9	11
6	10	20	20
6	12	23	22
6	13	14	13
7	0	12	12
7	2	8	4
7	7	17	17
7	8	22	22
7	9	14	15
7	10	15	14
8	2	14	16
8	3	13	13
8	5	10	4
8	7	12	9
8	9	23	23
8	10	8	3
8	11	17	18
9	5	18	18
9	7	8	7
9	9	9	8
9	10	12	12
	H= -4		
0	8	45	42
0	10	13	13
0	12	12	6
1	0	9	7
1	3	26	25
1	4	20	21
1	5	41	41
1	6	12	13
1	9	15	15
1	12	9	10
1	13	21	21
2	1	26	24
2	3	25	25
2	4	22	22
2	6	54	55
2	7	21	23
2	8	8	8
2	10	9	10
2	13	10	10
3	0	16	12
3	1	13	15
3	2	23	23
3	3	25	25
3	7	29	29
3	8	35	34
3	10	8	10
3	12	21	20
3	14	15	13
4	0	16	14
4	1	19	22
4	2	17	15
4	3	18	15
4	4	21	23
4	7	20	21
4	10	11	14
4	13	9	10
5	0	16	16
5	1	17	16
5	3	28	28
5	5	14	18
5	6	15	17
5	7	11	11
5	8	8	9
5	11	11	11
5	12	8	3
5	13	17	17
6	1	15	17
6	2	12	7
6	4	12	15
6	5	13	14
6	6	20	19
6	7	7	5
6	8	8	5
6	12	17	17
6	13	11	13
7	0	8	6
7	2	10	8
7	3	11	7
7	4	7	7
7	6	8	7

K	L	FO	FC
7	7	3	5
7	10	19	19
7	11	16	18
8	4	10	13
8	5	3	6
8	6	14	18
8	8	11	12
8	10	8	5
8	11	24	25
9	0	12	12
9	2	25	25
9	3	13	12
9	4	10	8
9	5	8	5
9	6	14	15
9	7	16	20
9	8	12	7
9	9	15	14
10	0	15	13
10	1	8	8
10	3	3	3
10	4	19	20
10	5	8	11
10	7	10	13
10	8	12	10
10	9	8	3
11	3	19	18
11	4	3	6
11	6	9	6
11	8	9	6

H= -3

K	L	FO	FC
0	2	43	42
0	4	18	19
0	6	7	4
0	8	20	20
0	12	15	16
1	0	15	13
1	1	21	21
1	2	22	23
1	3	17	15
1	4	12	10
1	5	67	73
1	6	33	32
1	7	24	23
1	8	10	10
1	9	16	17
1	14	3	3
2	0	11	9
2	1	29	31
2	2	8	7
2	3	23	26
2	5	50	52
2	7	24	29
2	9	43	45

K	L	FO	FC
2	3	9	10
2	10	14	12
2	11	3	7
3	1	21	19
3	3	14	14
3	4	41	39
3	6	8	9
3	7	17	17
3	8	19	19
3	9	19	19
3	10	20	20
3	12	17	17
4	0	12	11
4	1	11	11
4	3	23	22
4	4	7	7
4	5	25	24
4	6	18	18
4	7	9	7
4	8	8	8
4	11	12	13
4	12	9	3
5	0	12	11
5	1	19	20
5	2	43	42
5	4	13	12
5	5	28	29
5	6	13	12
5	7	16	19
5	9	16	15
5	10	7	2
5	11	8	8
5	13	14	15
6	0	35	36
6	1	16	14
6	3	29	29
6	4	17	19
6	5	16	15
6	6	24	26
6	7	8	9
6	8	10	9
6	9	14	13
6	12	9	5
7	0	23	23
7	1	11	10
7	2	7	9
7	3	16	15
7	4	20	18
7	5	22	22
7	6	9	9
7	8	10	9
7	10	13	12
7	11	10	2
8	1	19	20
8	2	7	2
8	4	9	8

K	L	FO	FC
8	5	7	3
8	6	11	14
8	7	10	10
8	9	9	10
8	11	11	5
9	0	9	12
9	2	16	15
9	3	17	18
9	4	25	26
9	7	8	1
9	8	9	7
9	9	15	15
9	10	15	16
10	0	21	23
10	3	11	12
10	6	25	26
11	3	10	7
11	5	3	7
12	1	9	6
12	4	13	13
12	0	22	22

H= -2

K	L	FO	FC
0	6	10	10
0	8	22	23
0	10	17	16
0	12	13	10
1	0	24	25
1	1	27	24
1	2	22	16
1	4	61	54
1	7	26	25
1	8	19	16
1	9	41	42
1	10	12	11
2	1	7	5
2	2	37	40
2	4	62	60
2	5	33	36
2	7	12	10
2	8	8	8
2	9	17	16
2	10	16	18
2	11	8	7
2	12	8	7
2	13	9	8
3	0	6	10
3	1	23	24
3	2	9	8
3	3	34	29
3	4	28	29
3	5	9	9
3	7	15	13
3	8	19	13
3	9	7	8

K	L	FO	FC
3	10	10	8
3	11	13	12
3	12	20	20
3	13	9	1
4	0	7	9
4	1	22	25
4	2	36	33
4	3	37	40
4	4	14	14
4	5	30	29
4	6	6	4
4	7	7	10
4	8	14	13
4	9	7	1
4	11	13	13
5	0	10	6
5	1	33	32
5	2	10	7
5	4	52	48
5	5	13	15
5	6	10	8
5	7	25	25
5	9	14	13
5	0	25	25
6	2	53	53
6	3	25	23
6	4	10	4
6	5	19	18
6	6	23	23
6	7	22	19
6	8	27	28
7	0	7	6
7	1	8	7
7	2	19	19
7	4	25	25
7	5	29	30
7	6	17	17
7	7	11	10
7	8	19	17
7	9	8	4
7	10	10	10
8	0	9	9
8	1	12	11
8	3	28	29
8	4	13	14
8	7	7	7
8	9	22	23
9	0	13	14
9	1	9	8
9	2	16	19
9	4	21	19
9	5	16	15
9	6	9	9
9	7	16	15
10	0	10	11
10	1	9	7

K	L	FO	FC
10	3	10	15
10	4	11	9
10	8	23	24
11	0	17	16
11	5	13	13
11	7	12	11
12	1	10	9
12	4	13	11
12	6	18	20
13	1	9	7
13	3	12	10
13	4	13	13
	H=	-1	
0	6	6	3
0	8	25	28
0	10	7	4
0	12	13	13
1	4	14	14
1	5	22	23
1	6	22	21
1	7	16	18
1	9	10	16
1	11	15	16
1	12	12	9
2	1	9	10
2	2	6	6
2	3	16	15
2	4	30	29
2	6	11	15
2	7	15	15
2	8	26	26
2	9	8	4
2	11	15	15
3	2	6	12
3	3	22	19
3	4	19	18
3	5	19	17
3	6	14	13
3	7	9	0
3	9	7	8
3	10	16	15
3	12	9	5
4	0	57	52
4	3	21	23
4	4	36	35
4	5	26	28
4	6	17	18
4	7	22	24
4	10	11	10
4	11	15	16
4	12	10	7
5	0	12	14
5	1	25	28
5	2	11	4
5	3	17	19
5	5	8	7
5	6	18	17
5	7	19	17
5	8	19	18
5	9	27	25
5	10	11	10
6	2	9	10
6	3	13	14
6	4	30	30
6	5	37	37
6	6	8	6
6	8	22	21
6	10	20	19
7	3	29	29
7	4	6	6
7	5	7	8
7	6	26	26
7	7	17	19
7	9	10	5
8	0	16	16
8	2	7	4
8	5	18	16
8	6	7	5
9	1	7	10
9	2	31	29
9	3	11	12
9	6	24	24
9	7	12	12
9	9	9	8
10	0	18	20
10	1	22	21
10	2	17	16
10	3	10	10
10	4	8	5
10	6	9	6
11	0	8	5
11	1	14	16
11	7	17	15
12	1	12	11
12	3	16	17
12	5	10	8
13	0	9	7
13	1	15	14
13	3	16	12
	H=	0	
0	2	19	26
0	4	17	16
0	6	19	18
0	8	11	13
0	10	11	11
1	4	64	62
1	7	12	12
1	9	9	12
1	10	11	8
2	0	20	25
2	3	38	41
2	4	13	11
2	5	23	23
2	6	16	19
2	7	6	6
2	8	8	9
2	9	9	4
2	10	8	10
3	1	25	23
3	3	22	22
3	4	9	14
3	5	33	31
3	7	14	15
3	8	12	11
4	0	40	34
4	2	29	26
4	3	35	35
4	5	8	6
4	6	16	16
4	7	17	17
4	8	14	14
5	1	37	35
5	2	24	24
5	5	8	8
5	8	14	15
5	9	20	20
6	0	70	63
6	1	7	5
6	3	15	15
6	5	23	22
6	7	14	10
6	8	9	4
6	9	8	5
6	10	13	12
7	1	38	36
7	2	11	14
7	3	11	10
7	4	18	17
7	5	22	22
7	7	8	11
7	9	11	10
8	0	20	17
8	1	39	36
8	2	14	14
8	4	9	7
8	5	21	20
9	1	11	5
9	2	23	24
9	4	20	19
9	5	17	18
9	6	9	8
9	8	9	5
10	0	9	6
10	1	21	24
10	2	7	13
10	3	10	15
10	4	11	12
10	5	10	8
10	6	12	11
11	1	40	41
11	2	12	11
11	3	18	17
11	4	13	11
11	5	14	15
12	0	8	3
12	2	13	11
12	3	10	11
12	4	10	8
12	5	18	18
	H=	1	
0	8	23	25
0	10	9	4
1	1	12	15
1	2	29	28
1	3	16	16
1	10	8	0
2	2	26	30
2	3	32	33
2	8	8	9
2	9	13	13
3	1	26	24
3	2	11	11
3	3	13	14
4	0	61	52
4	1	10	2
4	2	26	28
4	7	11	12
4	8	19	17
5	0	11	14
5	1	35	34
5	2	7	4
5	3	13	15
6	0	6	5
6	2	29	28
6	8	9	8
6	9	15	16
7	1	15	17
7	2	17	13
7	7	15	16
8	0	16	16
8	1	22	21
8	2	7	6
8	5	11	13
9	6	11	13
9	1	7	6
9	3	8	6
9	4	26	26
9	5	10	5

K	L	FO	FC
9	6	12	13
10	0	19	20
10	2	16	15
10	3	11	13
10	4	11	9
10	5	18	18
10	6	11	10
11	1	40	41
11	3	35	33
12	1	9	6
12	3	18	16
	H=	2	
0	6	23	23
0	8	8	6
1	6	24	24
1	7	10	10
1	8	10	8
2	6	10	11
2	7	10	11
2	8	8	6
3	6	23	24
3	7	9	6
4	6	8	3
4	8	9	8
5	5	13	15
5	6	10	11
6	5	10	10
7	4	10	10
7	5	11	15
8	4	9	9
8	5	14	16
9	1	10	9
9	3	19	18
10	0	13	11
10	1	7	11
11	0	13	16
11	1	30	28
11	3	18	19
12	1	10	15
	H=	3	
0	6	14	19
2	4	9	12
2	5	11	16
4	4	14	17
4	5	16	18
5	3	11	7
5	5	9	8
6	3	9	4
6	4	12	8
7	3	13	12
7	4	13	14
8	0	7	9

K	L	FO	FC
8	4	8	5
9	0	14	12
9	3	5	3
10	0	23	23
	H=	4	
0	2	17	21
0	4	10	7
1	2	10	12
1	3	9	10
3	3	9	8
3	4	16	17
4	3	9	5
5	1	13	11
5	3	16	15
6	1	14	15
6	2	15	15
8	1	10	14
9	0	14	12
10	0	9	13
	H=	5	
1	1	12	16
2	1	21	23
3	0	13	15
4	0	8	7
4	1	16	19
7	0	11	12
	H=	6	
3	0	11	10

Structure Factor Table For S,S-Dibromo-

1,3-Dimethylimidazole-2-Thione

K	L	FO	FC
	H=	0	
-16	-3	22	6
-16	-2	27	21
-16	2	29	21
-15	-3	26	19
-15	-1	39	31
-15	1	42	31
-15	3	25	19
-14	-11	33	35
-14	-8	30	32
-14	-6	67	53
-14	-2	23	17
-14	6	67	53
-14	8	30	32
-14	11	37	35
-13	-11	31	25
-13	-4	72	64
-13	-2	23	25
-13	2	20	25
-13	4	73	64
-13	11	33	25
-12	-5	65	58
-12	-4	35	34
-12	-3	61	60
-12	-2	70	66
-12	0	30	37
-12	2	66	66
-12	3	62	60
-12	4	36	34
-12	5	62	58
-11	-12	34	39
-11	-9	24	22
-11	-8	41	39
-11	-7	27	19
-11	-5	103	99
-11	-4	29	28
-11	-2	22	25
-11	2	21	25
-11	4	29	28
-11	5	103	99
-11	6	21	22
-11	7	25	19
-11	8	41	39
-11	12	34	39
-10	-13	52	50
-10	-12	71	67
-10	-9	49	50
-10	-5	90	85
-10	-4	31	30
-10	-1	33	30
-10	0	85	77
-10	1	34	30
-10	3	17	16
-10	4	32	30
-10	5	86	85
-10	9	47	50
-10	12	64	67
-10	13	41	50
-9	-15	24	29
-9	-13	34	27
-9	-10	51	45
-9	-9	50	51
-9	-7	32	32
-9	-6	27	29
-9	-5	31	31
-9	-3	83	84
-9	-2	33	36
-9	-1	62	63
-9	1	62	63
-9	2	34	36
-9	3	81	84
-9	5	35	31
-9	6	20	28
-9	7	32	32
-9	9	47	51
-9	10	43	45
-9	13	27	27
-8	-17	26	18
-8	-14	24	26
-8	-13	86	89
-8	-12	53	51
-8	-11	57	56
-8	-9	50	49
-8	-8	37	35
-8	-7	41	34
-8	-6	58	56
-8	-5	53	50
-8	-4	103	101
-8	-3	63	65
-8	-2	16	16
-8	-1	110	119
-8	0	25	28
-8	1	109	119
-8	2	18	16
-8	3	59	65
-8	4	103	101
-8	5	50	50
-8	6	53	56
-8	7	37	34
-8	8	34	35
-8	9	47	49
-8	11	55	56
-8	12	50	51
-8	13	82	89
-7	-14	45	48
-7	-12	52	49
-7	-11	52	51
-7	-9	32	34
-7	-8	54	49
-7	-7	64	63
-7	-6	104	100
-7	-5	96	94
-7	-4	38	40
-7	-3	39	40
-7	-2	94	98
-7	-1	68	69
-7	1	68	69
-7	2	69	98
-7	3	34	40
-7	4	33	40
-7	5	87	94
-7	6	95	100
-7	7	59	63
-7	8	49	49
-7	9	30	34
-7	11	49	51
-7	12	49	49
-7	14	43	48
-6	-16	36	43
-6	-16	36	45
-6	-12	21	19
-6	-11	25	23
-6	-10	63	60
-6	-7	85	81
-6	-6	61	62
-6	-5	130	126
-6	-4	28	28
-6	-3	105	109
-6	-2	149	169
-6	-1	41	46
-6	0	20	23
-6	1	42	46
-6	2	138	169
-6	3	98	109
-6	4	25	28
-6	5	117	126
-6	6	57	62
-6	7	81	81
-6	10	60	60
-6	16	37	45
-6	18	34	43
-5	-15	70	79
-5	-14	33	38
-5	-13	70	69
-5	-12	46	46
-5	-11	49	46
-5	-9	61	58
-5	-8	94	87
-5	-7	68	65
-5	-6	25	24
-5	-5	39	40
-5	-4	98	93
-5	-3	145	148
-5	-2	51	59
-5	-1	26	33
-5	1	27	33
-5	2	46	59
-5	3	133	143
-5	4	88	93
-5	5	34	40
-5	6	23	24
-5	7	64	65
-5	8	89	87
-5	9	58	58
-5	11	48	46
-5	12	48	46
-5	13	67	69
-5	14	34	34
-5	15	67	79
-5	17	24	23
-4	-18	39	44
-4	-15	46	50
-4	-14	30	34
-4	-13	29	29
-4	-11	53	52
-4	-10	28	27
-4	-8	88	85
-4	-7	150	135
-4	-6	222	212
-4	-5	39	35
-4	-4	20	18
-4	-3	91	93
-4	-2	12	14
-4	-1	32	33
-4	0	79	87
-4	1	33	33
-4	2	14	14
-4	3	84	93
-4	4	17	18
-4	5	39	35
-4	6	211	212
-4	7	143	135
-4	8	83	85
-4	10	29	27
-4	11	53	52
-4	13	30	29
-4	14	25	34
-4	15	45	50
-4	18	34	44
-3	-18	39	51
-3	-17	41	48
-3	-16	66	70
-3	-14	40	41
-3	-11	96	96
-3	-10	27	24
-3	-9	16	18
-3	-8	70	66
-3	-7	21	23
-3	-6	36	29
-3	-5	23	14
-3	-4	145	132
-3	-3	69	58
-3	-2	88	98

K	L	FO	FC
-3	-1	224	273
-3	1	206	273
-3	2	77	98
-3	3	64	58
-3	4	136	132
-3	5	22	14
-3	6	36	28
-3	7	22	23
-3	8	69	66
-3	10	24	24
-3	11	94	96
-3	14	35	41
-3	16	61	70
-3	17	42	46
-3	18	44	51
-2	-17	30	36
-2	-16	49	58
-2	-15	25	27
-2	-14	34	33
-2	-12	33	31
-2	-11	112	110
-2	-10	128	119
-2	-9	98	90
-2	-8	191	180
-2	-6	36	31
-2	-5	91	77
-2	-4	270	244
-2	-3	136	135
-2	-2	12	16
-2	-1	58	65
-2	0	41	42
-2	1	51	65
-2	2	10	16
-2	3	128	135
-2	4	257	244
-2	5	89	77
-2	6	37	31
-2	8	190	185
-2	9	96	90
-2	10	125	119
-2	11	109	110
-2	12	31	31
-2	14	34	33
-2	15	23	27
-2	16	43	38
-2	17	32	36
-1	-16	25	27
-1	-17	46	53
-1	-16	33	31
-1	-15	34	32
-1	-14	25	28
-1	-13	19	24
-1	-11	23	28
-1	-10	174	172
-1	-9	94	92
-1	-8	43	36
-1	-7	177	162
-1	-6	62	55
-1	-5	174	144
-1	-4	134	118
-1	-3	72	64
-1	-2	71	62
-1	2	68	62
-1	3	70	64
-1	4	131	118
-1	5	172	144
-1	6	62	55
-1	7	175	162
-1	8	45	36
-1	9	93	92
-1	10	176	172
-1	11	31	28
-1	13	21	24
-1	14	25	26
-1	15	30	32
-1	16	29	31
-1	17	45	53
0	-13	35	38
0	-16	28	31
0	-14	61	64
0	-12	99	103
0	-10	51	46
0	-8	62	60
0	-6	20	16
0	-4	38	35
0	-2	66	55
0	2	68	55
0	4	39	25
0	6	19	16
0	8	65	60
0	10	49	46
0	12	142	103
0	14	59	64
0	16	31	31
0	18	29	38

H= 1

K	L	FO	FC
-16	-6	31	29
-16	1	30	22
-16	4	31	23
-15	-3	26	19
-15	1	22	16
-15	2	23	15
-15	4	24	17
-15	9	33	17
-14	-5	34	27
-14	-3	27	31
-14	0	69	60
-14	2	29	23
-14	8	28	19
-13	-10	49	39
-13	-7	21	16
-13	-4	37	36
-13	2	52	44
-13	5	32	21
-13	7	29	27
-13	10	49	44
-12	-13	25	27
-12	-11	49	47
-12	-10	25	23
-12	-8	29	23
-12	-5	41	35
-12	-3	55	46
-12	-2	40	33
-12	-1	27	22
-12	0	35	29
-12	1	41	32
-12	3	21	20
-12	4	57	48
-12	5	36	38
-12	8	29	24
-12	9	27	22
-12	10	32	35
-12	11	33	36
-11	-9	33	29
-11	-7	19	13
-11	-6	56	55
-11	-4	35	42
-11	-2	23	20
-11	-1	55	50
-11	1	45	43
-11	2	40	38
-11	3	48	46
-11	4	40	36
-11	5	21	19
-11	6	37	41
-11	7	45	45
-11	10	27	21
-11	11	44	45
-10	-14	43	46
-10	-11	64	63
-10	-10	27	25
-10	-9	24	20
-10	-8	24	21
-10	-7	45	37
-10	-6	99	90
-10	-4	63	58
-10	-3	91	92
-10	-1	29	32
-10	0	23	25
-10	1	67	61
-10	5	45	39
-10	6	61	58
-10	7	39	35
-10	8	20	17
-10	10	31	28
-10	13	25	23
-9	-16	29	29
-9	-13	35	34
-9	-12	27	24
-9	-9	20	13
-9	-7	45	37
-9	-6	22	15
-9	-5	47	45
-9	-4	68	63
-9	-3	24	21
-9	1	43	44
-9	2	25	23
-9	3	103	106
-9	5	29	30
-9	7	44	43
-9	8	32	33
-9	11	34	34
-9	15	52	57
-8	-16	37	38
-8	-9	34	32
-8	-8	22	16
-8	-7	110	107
-8	-6	92	90
-8	-5	60	61
-8	-4	61	57
-8	-3	109	114
-8	-2	86	84
-8	0	26	33
-8	2	29	32
-8	3	41	43
-8	4	22	15
-8	5	123	130
-8	7	72	82
-8	8	51	49
-8	10	64	61
-8	13	25	28
-8	15	30	27
-7	-17	26	31
-7	-16	36	34
-7	-15	34	38
-7	-14	23	21
-7	-12	40	38
-7	-10	21	18
-7	-8	58	54
-7	-7	75	70
-7	-6	66	67
-7	-5	63	65
-7	-3	101	102
-7	-2	89	93
-7	-1	49	45
-7	0	75	74
-7	3	40	43
-7	4	116	123
-7	5	61	57
-7	7	36	41
-7	8	72	77
-7	9	28	28

K	L	FO	FC
-7	10	37	37
-7	11	41	44
-7	13	50	52
-7	17	37	41
-6	-14	60	62
-6	-13	76	76
-6	-12	94	97
-6	-11	65	67
-6	-10	42	45
-6	-9	42	35
-6	-8	124	114
-6	-7	56	51
-6	-6	25	26
-6	-5	66	63
-6	-3	40	44
-6	-2	18	12
-6	-1	99	112
-6	0	29	33
-6	1	64	70
-6	2	41	46
-6	3	52	63
-6	4	167	159
-5	5	39	42
-6	6	29	28
-6	7	70	72
-6	8	89	91
-6	9	24	24
-6	10	60	56
-6	11	50	48
-6	12	20	19
-6	13	71	73
-6	14	50	54
-6	16	50	55
-5	-17	51	56
-5	-13	59	61
-5	-12	20	19
-5	-11	77	77
-5	-9	23	23
-5	-7	157	147
-5	-6	39	39
-5	-5	32	32
-5	-4	54	54
-5	-3	149	150
-5	-2	113	119
-5	-1	57	65
-5	0	26	25
-5	1	18	23
-5	2	53	56
-5	3	52	57
-5	4	22	21
-5	5	52	48
-5	6	46	44
-5	7	23	26
-5	9	193	200
-5	10	49	50
-5	11	35	33
-5	12	38	34
-5	13	34	34
-5	14	36	35
-3	12	38	34
-3	14	28	35
-4	-14	23	32
-4	-13	37	41
-4	-12	99	98
-4	-11	22	18
-4	-10	32	30
-4	-9	129	121
-4	-8	77	69
-4	-7	42	38
-4	-6	77	72
-4	-5	121	109
-4	-4	62	61
-4	-3	46	49
-4	-1	245	288
-4	0	237	280
-4	1	36	35
-4	2	157	185
-4	3	95	99
-4	4	30	31
-4	8	43	44
-4	9	20	20
-4	11	28	23
-4	12	83	86
-4	13	48	56
-4	14	53	57
-4	16	30	29
-3	-17	26	27
-3	-15	66	76
-3	-13	62	63
-3	-12	65	67
-3	-11	82	87
-3	-10	115	112
-3	-9	33	29
-3	-8	104	143
-3	-7	34	31
-3	-6	27	23
-3	-5	123	105
-3	-4	99	94
-3	-3	159	145
-3	-2	153	158
-3	-1	66	73
-3	0	24	29
-3	1	78	97
-3	2	96	87
-3	3	109	104
-3	4	40	41
-3	5	202	194
-3	6	24	19
-3	7	56	50
-3	8	59	56
-3	9	21	23
-3	10	64	63
-3	12	31	38
-3	13	34	34
-3	14	36	35
-3	15	39	42
-3	16	29	32
-3	17	52	54
-2	-19	27	38
-2	-18	50	64
-2	-17	31	34
-2	-16	25	33
-2	-14	61	64
-2	-11	31	32
-2	-9	90	85
-2	-8	178	166
-2	-7	17	17
-2	-6	35	33
-2	-5	157	145
-2	-4	125	100
-2	-2	188	209
-2	-1	15	17
-2	0	77	93
-2	1	70	81
-2	2	168	183
-2	3	153	142
-2	4	47	51
-2	5	138	126
-2	6	60	53
-2	7	110	103
-2	8	49	47
-2	9	40	42
-2	10	174	167
-2	11	31	32
-2	16	48	55
-1	-19	35	40
-1	-18	24	37
-1	-16	59	66
-1	-13	62	62
-1	-11	56	53
-1	-10	51	49
-1	-9	170	158
-1	-8	97	92
-1	-7	57	49
-1	-6	75	63
-1	-5	76	64
-1	-4	146	126
-1	-3	49	43
-1	-2	87	79
-1	-1	84	84
-1	0	92	126
-1	1	23	19
-1	2	185	178
-1	3	16	15
-1	4	154	125
-1	5	66	59
-1	6	32	28
-1	7	46	38
-1	8	26	24
-1	9	38	36
-1	11	80	78
-1	12	59	63
-1	13	51	51
-1	14	35	31
-1	15	93	103
-1	16	34	49
0	-18	48	48
0	-16	53	59
0	-14	50	58
0	-12	66	71
0	-10	18	14
0	-8	103	99
0	-6	261	246
0	-4	89	73
0	-2	165	148
0	0	13	13
0	2	133	121
0	4	39	25
0	6	389	362
0	8	162	148
0	10	24	26
0	12	39	38
0	16	46	48
0	18	47	49

H= 2

K	L	FO	FC
-16	-2	25	23
-16	0	30	28
-16	4	34	24
-15	-6	24	15
-15	0	27	16
-15	5	26	18
-15	7	24	21
-14	-8	41	36
-14	-7	22	14
-14	-6	41	38
-14	-4	48	34
-14	-2	25	21
-14	1	36	33
-14	2	26	25
-14	6	29	24
-14	7	32	21
-14	8	31	27
-13	-5	21	14
-13	-4	37	34
-13	2	53	54
-13	3	30	24
-13	8	38	29
-12	-9	53	45
-12	-8	62	54
-12	-7	50	39
-12	-5	24	23
-12	-4	27	30
-12	-3	21	25
-12	-2	35	34
-12	-1	34	35

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC
-12	1	40	34	-9	-6	58	55	-6	10	109	107	-3	-14	39	44
-12	4	43	35	-8	-4	70	72	-6	11	29	26	-3	-13	23	27
-12	5	38	32	-8	-3	33	31	-6	12	38	42	-3	-12	40	41
-12	6	45	42	-8	-2	63	64	-6	13	26	24	-3	-11	27	26
-12	7	47	34	-8	-1	169	186	-5	-17	60	66	-3	-10	59	52
-12	8	26	28	-8	0	48	52	-5	-14	26	29	-3	-9	185	176
-11	-11	38	38	-8	1	67	76	-5	-13	79	80	-3	-7	162	145
-11	-10	27	29	-8	2	80	88	-5	-11	19	17	-3	-6	139	126
-11	-5	24	15	-8	3	51	54	-5	-10	32	28	-3	-5	55	53
-11	-3	85	84	-8	4	20	19	-5	-9	34	31	-3	-4	119	110
-11	-2	36	38	-8	9	33	30	-5	-8	23	21	-3	-3	64	65
-11	-1	35	38	-8	11	38	41	-5	-7	19	17	-3	-2	83	89
-11	0	42	45	-8	13	41	44	-5	-6	39	35	-3	-1	13	18
-11	1	48	49	-8	14	37	40	-5	-5	128	132	-3	1	45	50
-11	6	27	28	-8	16	29	25	-5	-3	20	15	-3	2	29	32
-11	8	39	39	-7	-15	31	33	-5	-2	83	94	-3	3	117	115
-11	9	23	24	-7	-15	41	40	-5	-1	82	93	-3	4	165	156
-11	10	33	39	-7	-11	47	44	-5	0	50	57	-3	5	19	14
-11	13	24	29	-7	-10	21	24	-5	1	49	56	-3	6	86	79
-10	-11	36	33	-7	-9	75	71	-5	2	43	46	-3	7	185	175
-10	-9	44	41	-7	-8	53	51	-5	3	166	188	-3	8	44	43
-10	-8	67	62	-7	-6	47	43	-5	5	17	13	-3	9	39	39
-10	-6	35	32	-7	-5	17	15	-5	6	29	36	-3	10	56	55
-10	-5	56	55	-7	-4	21	26	-5	7	65	61	-3	11	87	90
-10	-4	39	35	-7	-3	40	44	-5	8	31	28	-3	12	45	49
-10	-2	35	38	-7	-2	92	98	-5	15	82	93	-3	14	51	54
-10	-1	79	79	-7	-1	49	52	-5	17	30	30	-3	16	24	31
-10	0	65	64	-7	0	79	85	-4	-17	49	54	-2	-19	49	57
-10	1	20	17	-7	1	57	64	-4	-16	30	31	-2	-16	30	31
-10	2	91	94	-7	2	19	21	-4	-14	27	31	-2	-14	78	88
-10	3	56	60	-7	3	94	102	-4	-12	32	33	-2	-13	75	76
-10	4	30	29	-7	4	83	83	-4	-11	30	25	-2	-12	20	15
-10	6	26	24	-7	6	49	50	-4	-10	40	35	-2	-11	63	62
-10	7	80	80	-7	7	43	44	-4	-8	70	63	-2	-9	31	29
-9	-15	25	24	-7	10	48	51	-4	-7	99	89	-2	-8	85	77
-9	-11	79	79	-7	16	28	25	-4	-6	95	91	-2	-7	16	13
-9	-10	43	43	-6	-18	31	31	-4	-5	38	36	-2	-6	176	154
-9	-8	22	16	-6	-16	23	1	-4	-4	184	187	-2	-5	52	53
-9	-7	81	79	-6	-14	30	35	-4	-3	136	140	-2	-4	22	19
-9	-4	23	22	-6	-12	98	90	-4	-2	90	99	-2	-3	191	179
-9	-3	17	15	-6	-11	45	47	-4	0	38	46	-2	-2	141	154
-9	-1	38	43	-6	-10	54	51	-4	1	114	142	-2	0	29	29
-9	0	34	33	-6	-9	96	93	-4	2	116	132	-2	1	154	165
-9	1	32	35	-6	-8	88	85	-4	3	21	20	-2	3	142	129
-9	2	27	26	-6	-7	118	119	-4	4	37	37	-2	4	254	247
-9	8	42	45	-6	-6	71	68	-4	5	182	183	-2	6	132	121
-9	9	127	131	-6	-5	87	91	-4	6	90	89	-2	7	77	72
-8	-16	43	42	-6	-4	44	47	-4	7	46	40	-2	8	20	18
-8	-15	29	34	-6	-3	72	74	-4	8	95	91	-2	9	50	52
-8	-14	25	18	-6	-2	78	82	-4	9	59	56	-2	10	47	45
-8	-13	40	39	-6	0	59	71	-4	10	26	25	-2	11	55	52
-8	-12	37	39	-6	1	46	50	-4	11	34	35	-2	12	53	55
-8	-11	54	50	-6	5	75	78	-4	12	39	44	-2	13	60	64
-8	-10	49	47	-6	7	70	70	-4	13	47	45	-2	14	67	65
-8	-9	35	30	-6	8	90	93	-4	14	24	25	-2	15	24	26
-8	-8	40	39	-6	9	40	42	-3	-16	48	52	-2	17	27	28

K	L	FO	FC
-1	-16	49	56
-1	-15	60	64
-1	-13	82	86
-1	-12	69	69
-1	-11	40	41
-1	-10	68	66
-1	-9	30	25
-1	-8	90	79
-1	-7	41	37
-1	-6	107	86
-1	-5	31	24
-1	-4	190	172
-1	-3	353	331
-1	-2	83	66
-1	-1	19	24
-1	0	70	77
-1	1	114	105
-1	2	213	197
-1	3	133	114
-1	4	72	63
-1	5	54	53
-1	6	76	68
-1	7	45	35
-1	8	96	90
-1	9	71	71
-1	10	24	25
-1	12	35	36
-1	13	83	90
0	-14	78	85
0	-12	66	65
0	-10	171	167
0	-8	170	156
0	-6	197	183
0	-4	105	95
0	-2	111	98
0	0	230	208
0	2	365	322
0	4	53	57
0	6	192	175
0	8	129	119
0	10	20	10
0	12	122	123
0	14	74	80
0	16	30	36

H= 3

K	L	FO	FC
-15	-3	27	20
-14	-10	24	18
-14	-4	23	18
-14	-2	59	52
-14	0	27	25
-14	2	43	38
-14	7	25	17
-13	-10	25	20
-13	-8	52	44
-13	7	30	24
-13	8	47	45
-12	-6	35	33
-12	-3	21	21
-12	-2	51	42
-12	-1	56	49
-12	0	25	28
-12	1	47	45
-12	6	24	17
-11	-9	80	74
-11	-6	25	19
-11	-4	40	44
-11	-1	39	37
-11	1	41	32
-11	3	29	17
-11	4	36	28
-11	7	21	24
-11	9	23	20
-10	-10	40	40
-10	-9	69	64
-10	-8	50	49
-10	-7	26	31
-10	-5	32	29
-10	-4	32	31
-10	-3	22	20
-10	-2	34	35
-10	-1	29	37
-10	0	66	67
-10	1	69	73
-10	4	45	47
-10	6	21	27
-10	7	24	22
-10	8	49	52
-10	9	57	57
-10	12	27	27
-9	-14	37	31
-9	-13	23	13
-9	-7	52	45
-9	-5	60	54
-9	-4	29	23
-9	-2	31	28
-9	-1	43	42
-9	0	19	14
-9	1	19	20
-9	2	46	51
-9	3	26	29
-9	7	71	67
-9	11	26	32
-8	-13	28	20
-8	-10	84	82
-8	-9	73	70
-8	-8	27	26
-8	-7	93	87
-8	-5	70	71
-8	-1	20	25
-8	0	128	138
-8	1	36	41
-8	2	33	34
-8	3	32	33
-8	5	100	105
-8	6	19	14
-8	7	53	55
-8	8	35	36
-8	9	39	41
-8	12	22	14
-7	-16	38	41
-7	-15	53	55
-7	-10	89	87
-7	-9	76	76
-7	-8	23	16
-7	-7	54	49
-7	-5	32	31
-7	-4	52	55
-7	-3	61	65
-7	-2	34	37
-7	-1	61	65
-7	0	33	39
-7	1	84	89
-7	2	15	8
-7	3	33	34
-7	4	31	35
-7	6	29	30
-7	7	54	53
-7	10	81	86
-7	12	25	19
-7	13	34	40
-6	-15	36	39
-6	-11	36	35
-6	-10	29	26
-6	-8	34	35
-6	-7	32	31
-6	-6	150	151
-6	-5	51	54
-6	-4	70	72
-6	-3	93	100
-6	-2	51	57
-6	-1	110	125
-6	0	23	29
-6	1	109	125
-6	3	43	51
-6	4	20	22
-6	5	32	38
-6	6	123	130
-6	7	18	17
-6	8	45	46
-6	11	29	26
-6	14	29	37
-6	15	26	18
-5	-15	41	37
-5	-12	57	61
-5	-11	145	143
-5	-8	33	31
-5	-7	49	47
-5	-6	40	41
-5	-5	18	22
-5	-4	87	89
-5	-3	29	36
-5	-1	64	74
-5	0	19	24
-5	1	134	163
-5	2	33	40
-5	3	35	41
-5	4	55	57
-5	8	31	27
-5	9	94	92
-5	11	74	72
-5	12	25	20
-5	13	54	53
-4	-16	42	48
-4	-15	67	72
-4	-12	27	31
-4	-11	93	94
-4	-10	97	93
-4	-8	54	51
-4	-7	90	82
-4	-6	70	67
-4	-5	56	50
-4	-4	144	148
-4	-3	21	16
-4	-2	114	132
-4	-1	57	72
-4	1	49	53
-4	2	139	151
-4	3	41	41
-4	4	51	46
-4	5	50	44
-4	6	70	70
-4	7	77	72
-4	8	29	26
-4	9	33	33
-4	10	39	37
-4	11	89	86
-4	14	51	55
-4	15	24	18
-3	-17	29	32
-3	-15	56	59
-3	-14	52	56
-3	-12	45	48
-3	-11	19	19
-3	-10	53	54
-3	-9	20	17
-3	-7	68	65
-3	-5	117	111
-3	-4	126	116
-3	-3	181	191
-3	-2	69	75
-3	-1	19	20
-3	0	18	25

K	L	FO	FC	K	L	FO	FC	K	L	FC	FC	K	L	FO	FC
-3	1	19	23	-1	3	172	142	-10	-6	26	26	-7	5	30	31
-3	2	139	141	-1	4	42	39	-10	-4	56	57	-7	7	41	40
-3	3	35	30	-1	5	65	56	-10	-3	53	53	-7	8	29	27
-3	4	103	103	-1	6	108	95	-10	-2	69	67	-7	9	47	48
-3	5	70	65	-1	7	86	78	-10	0	26	27	-7	10	22	17
-3	6	34	29	-1	8	29	20	-10	1	47	44	-7	12	29	26
-3	7	52	51	-1	12	23	18	-10	2	25	26	-7	13	33	33
-3	8	62	58	-1	13	28	31	-10	3	33	29	-6	-14	26	33
-3	9	60	59	-1	14	59	60	-10	6	67	68	-6	-13	31	29
-3	10	48	49	-1	17	26	30	-10	8	22	20	-6	-12	43	42
-3	13	76	82	0	-14	52	53	-10	10	43	44	-6	-10	29	27
-2	-16	23	26	0	-10	85	79	-9	-13	23	25	-6	-9	45	46
-2	-14	65	66	0	-8	166	157	-9	-12	22	18	-6	-8	27	21
-2	-13	86	90	0	-4	305	278	-9	-11	49	48	-6	-7	59	58
-2	-12	140	137	0	-2	10	19	-9	-9	63	63	-6	-6	29	27
-2	-10	24	25	0	0	25	16	-9	-8	47	47	-6	-5	74	76
-2	-9	60	61	0	2	99	83	-9	-7	20	20	-6	0	140	166
-2	-7	127	115	0	4	222	197	-9	-6	20	19	-6	1	26	29
-2	-6	77	69	0	6	97	90	-9	-2	29	26	-6	2	41	45
-2	-5	71	65	0	8	144	134	-9	-1	46	46	-6	3	93	99
-2	-4	103	94	0	10	26	25	-9	0	21	26	-6	5	62	64
-2	-3	47	48	0	12	99	102	-9	1	65	67	-6	6	29	30
-2	-2	45	45	0	14	31	28	-9	3	24	31	-6	7	54	55
-2	-1	15	17					-9	5	28	30	-6	8	22	19
-2	0	151	187		H=	4		-9	11	37	36	-6	9	29	26
-2	1	34	35					-8	-15	28	33	-6	12	60	64
-2	2	59	53	-14	-8	33	28	-8	-13	36	38	-5	-17	38	50
-2	3	123	111	-14	-4	26	17	-8	-11	51	52	-5	-15	65	67
-2	4	98	88	-14	-2	41	34	-8	-9	22	24	-5	-12	25	24
-2	5	71	65	-13	-6	31	28	-8	-7	42	42	-5	-11	22	26
-2	6	84	77	-13	-4	21	14	-8	-6	30	26	-5	-10	50	45
-2	7	66	59	-13	-2	44	42	-8	-5	26	32	-5	-8	69	67
-2	8	33	33	-13	1	22	20	-8	-4	63	67	-5	-6	47	47
-2	9	54	49	-13	2	32	29	-8	-3	48	51	-5	-5	100	100
-2	10	47	45	-12	-7	44	36	-8	-2	28	33	-5	-3	21	22
-2	11	28	31	-12	-6	30	20	-8	-1	53	52	-5	-2	31	36
-2	12	121	124	-12	0	55	49	-8	1	69	73	-5	1	40	42
-2	13	54	55	-12	1	30	29	-8	3	33	31	-5	2	43	47
-1	-18	26	38	-12	4	28	23	-8	4	34	35	-5	3	36	40
-1	-17	36	43	-12	5	46	37	-8	5	38	41	-5	4	26	31
-1	-14	80	88	-12	6	30	28	-8	6	80	86	-5	5	109	110
-1	-12	20	25	-12	7	22	19	-8	11	58	57	-5	6	23	27
-1	-11	55	56	-12	8	24	20	-7	-16	32	33	-5	7	91	90
-1	-10	34	34	-11	-12	26	27	-7	-14	24	30	-5	9	56	52
-1	-9	82	79	-11	-11	33	30	-7	-13	34	35	-5	10	47	46
-1	-8	18	18	-11	-10	51	45	-7	-10	74	71	-5	11	32	37
-1	-7	40	38	-11	-7	32	21	-7	-9	28	27	-5	13	27	32
-1	-6	146	132	-11	-3	28	31	-7	-8	29	28	-4	-13	25	25
-1	-5	145	129	-11	-2	21	27	-7	-7	62	61	-4	-12	33	31
-1	-4	67	63	-11	-1	33	32	-7	-6	29	34	-4	-11	39	38
-1	-3	60	57	-11	2	21	25	-7	-5	47	43	-4	-10	92	91
-1	-2	33	31	-11	3	40	37	-7	-4	84	90	-4	-9	123	114
-1	-1	52	51	-11	5	29	30	-7	-1	52	59	-4	-8	96	93
-1	0	33	29	-11	6	22	25	-7	0	26	25	-4	-7	43	39
-1	1	24	25	-11	10	30	30	-7	2	37	41	-4	-5	147	143
-1	2	84	74	-10	-7	74	75	-7	4	45	47	-4	-4	85	87

K	L	FO	FC	K	L	FO	FC	K	L	FC	FC	K	L	FO	FC
-4	-2	37	-1	-2	1	50	47	-13	0	28	16	-7	3	34	37
-4	-1	61	73	-2	2	26	24	-13	1	27	17	-7	11	24	25
-4	0	55	67	-2	3	-6	43	-13	3	23	12	-6	-15	27	25
-4	1	20	26	-2	4	42	42	-12	-5	34	31	-6	-14	52	51
-4	2	30	27	-2	5	25	21	-12	2	28	18	-6	-13	49	51
-4	3	34	36	-2	6	182	170	-12	4	26	15	-6	-12	45	47
-4	4	151	149	-2	7	-1	35	-11	-11	25	25	-6	-11	37	40
-4	5	47	48	-2	9	71	71	-11	-7	38	38	-6	-8	50	52
-4	6	27	25	-2	10	65	63	-11	-4	40	38	-6	-7	39	43
-4	8	54	51	-2	11	52	50	-11	-3	36	34	-6	-6	31	36
-4	10	46	42	-2	12	33	35	-11	1	24	24	-6	-5	34	35
-4	12	43	50	-2	13	35	37	-11	4	29	27	-6	-4	42	45
-4	16	28	34	-2	14	25	29	-10	-12	27	26	-6	-3	67	78
-3	-17	32	38	-1	-13	62	62	-10	-8	37	37	-6	-2	64	71
-3	-16	34	37	-1	-12	108	111	-10	-5	44	44	-6	-1	34	38
-3	-15	41	51	-1	-11	69	70	-10	-1	50	50	-5	1	27	34
-3	-14	39	38	-1	-8	74	73	-10	0	20	19	-5	2	18	19
-3	-12	41	40	-1	-7	36	35	-10	3	55	53	-5	4	29	32
-3	-11	40	38	-1	-6	70	63	-10	4	62	60	-5	6	71	68
-3	-9	42	40	-1	-5	63	59	-10	11	24	17	-5	8	28	23
-3	-8	24	21	-1	-4	76	66	-9	-13	27	25	-6	9	32	30
-3	-7	53	45	-1	-3	63	57	-9	-7	32	30	-5	10	23	24
-3	-6	82	78	-1	-2	45	45	-9	-6	24	18	-5	11	46	46
-3	-5	41	35	-1	-1	37	46	-9	-5	28	29	-6	13	30	33
-3	-4	109	106	-1	0	52	51	-9	-3	58	61	-6	14	35	30
-3	-3	78	79	-1	1	121	109	-9	-2	22	27	-5	-13	23	22
-3	-2	19	23	-1	2	41	36	-9	2	23	22	-5	-12	26	25
-3	-1	94	115	-1	3	139	122	-9	4	28	25	-5	-11	35	34
-3	0	79	100	-1	4	53	46	-9	5	47	43	-5	-10	36	34
-3	1	90	97	-1	5	133	120	-9	6	20	6	-5	-9	114	111
-3	2	103	101	-1	8	89	82	-8	-11	31	29	-5	-7	59	55
-3	3	49	48	-1	9	22	24	-8	-10	25	22	-5	-6	58	58
-3	4	36	30	-1	10	42	41	-8	-9	24	26	-5	-5	18	17
-3	6	18	19	-1	11	68	68	-8	-8	56	51	-5	-4	32	34
-3	7	33	29	-1	15	35	38	-8	-7	45	45	-5	-2	20	20
-3	8	27	23	0	-18	27	28	-8	-6	49	48	-5	-1	21	27
-3	9	70	68	0	-16	91	105	-8	-5	84	85	-5	1	27	32
-3	10	57	59	0	-14	30	30	-8	-4	19	20	-5	2	35	36
-3	11	37	38	0	-12	54	55	-8	0	18	11	-5	3	75	79
-3	14	34	38	0	-10	53	50	-8	2	18	4	-5	4	39	41
-3	16	24	27	0	-8	124	109	-8	3	74	72	-5	5	47	50
-2	-19	26	22	0	-4	60	53	-8	4	44	40	-5	7	77	75
-2	-15	23	24	0	-2	249	262	-8	5	45	48	-5	8	35	29
-2	-14	49	45	0	0	25	32	-8	6	27	28	-5	11	46	49
-2	-13	86	97	0	2	190	173	-8	7	49	46	-4	-16	35	39
-2	-12	85	86	0	4	19	11	-8	11	24	16	-4	-14	42	43
-2	-10	26	27	0	10	122	120	-8	12	29	28	-4	-13	29	30
-2	-9	53	51	0	14	31	36	-7	-15	32	41	-4	-11	23	27
-2	-8	56	53					-7	-13	60	59	-4	-9	25	19
-2	-7	111	103		H=	5		-7	-10	26	25	-4	-8	78	72
-2	-6	186	175					-7	-7	83	83	-4	-6	53	54
-2	-5	56	49	-14	-2	37	31	-7	-6	79	82	-4	-3	87	95
-2	-4	23	26	-14	0	32	31	-7	-3	55	57	-4	-2	122	150
-2	-2	65	76	-14	3	25	18	-7	-1	17	21	-4	0	32	37
-2	-1	87	111	-13	-6	24	21	-7	0	19	18	-4	1	94	108
-2	0	75	85	-13	-2	22	21	-7	2	79	87	-4	4	21	22

K	L	FO	FC
-4	5	43	39
-4	9	33	31
-4	10	74	72
-3	-17	29	30
-3	-15	26	27
-3	-13	77	77
-3	-12	51	52
-3	-11	65	60
-3	-10	67	65
-3	-8	27	20
-3	-7	33	33
-3	-5	73	69
-3	-4	18	18
-3	-3	53	57
-3	-2	16	18
-3	-1	50	67
-3	0	24	33
-3	2	67	66
-3	3	93	88
-3	5	39	33
-3	6	30	28
-3	8	83	79
-3	10	44	49
-3	14	26	26
-3	15	47	56
-2	-10	59	58
-2	-9	27	22
-2	-8	60	57
-2	-7	112	99
-2	-6	97	89
-2	-4	48	46
-2	-3	51	49
-2	-2	55	64
-2	-1	65	79
-2	0	128	131
-2	2	99	93
-2	4	28	29
-2	5	90	84
-2	6	43	40
-2	8	73	65
-2	10	39	41
-2	11	27	23
-2	12	33	30
-2	14	28	24
-1	-17	41	49
-1	-16	37	47
-1	-15	45	39
-1	-12	24	24
-1	-11	22	20
-1	-10	44	42
-1	-9	35	35
-1	-7	91	79
-1	-6	72	67
-1	-5	34	33
-1	-3	63	59
-1	-2	95	97
-1	-1	84	79
-1	0	99	83
-1	1	41	36
-1	2	34	32
-1	3	22	22
-1	4	46	38
-1	5	43	37
-1	6	57	52
-1	7	21	19
-1	9	114	107
-1	11	25	27
-1	13	26	34
0	-14	46	55
0	-12	43	53
0	-10	154	149
0	-8	159	148
0	-6	124	112
0	-4	49	44
0	-2	49	66
0	0	25	25
0	2	18	15
0	4	138	119
0	6	55	52
0	8	66	62

H= 6

K	L	FO	FC
-13	2	28	20
-12	-6	33	27
-12	-5	28	29
-12	2	33	26
-12	5	26	22
-11	-7	23	8
-11	-5	57	52
-11	-4	24	20
-11	2	36	33
-10	-9	24	26
-10	-3	25	22
-10	-2	34	34
-10	0	22	23
-10	5	42	38
-9	-10	27	22
-9	-9	34	34
-9	-7	31	28
-9	3	55	55
-9	7	44	42
-8	-13	39	42
-8	-11	39	34
-8	-4	45	45
-8	-3	60	67
-8	-2	33	38
-8	1	33	34
-7	-13	35	42
-7	-12	33	30
-7	-11	33	31
-7	-7	35	35
-7	-6	22	26
-7	-5	29	34
-7	-4	28	29
-7	-3	30	34
-7	1	29	32
-7	2	55	58
-7	3	43	45
-7	8	29	24
-7	9	33	36
-6	-12	29	25
-6	-11	28	27
-6	-10	46	47
-6	-8	42	41
-6	-7	47	46
-6	-6	27	29
-6	-5	40	43
-6	-3	45	50
-6	-2	42	48
-6	-1	29	33
-6	0	35	39
-6	2	56	61
-6	3	44	45
-6	4	42	44
-6	5	43	46
-6	6	43	42
-6	8	47	45
-5	-15	53	59
-5	-12	28	28
-5	-10	32	28
-5	-8	41	37
-5	-7	36	38
-5	-3	79	92
-5	-2	30	38
-5	-1	40	49
-5	0	27	29
-5	1	43	46
-5	4	20	23
-5	9	54	51
-4	-15	34	40
-4	-14	24	24
-4	-11	53	53
-4	-9	28	28
-4	-8	80	76
-4	-7	43	39
-4	-6	74	74
-4	-5	31	32
-4	-4	29	36
-4	-2	27	29
-4	3	52	47
-4	4	75	72
-4	5	23	20
-4	6	49	50
-4	7	62	56
-3	-11	71	72
-3	-9	65	66
-3	-7	61	54
-3	-6	29	30
-3	-4	37	38
-3	-2	22	29
-3	1	70	72
-3	2	53	54
-3	3	30	27
-3	4	21	15
-3	6	38	34
-3	7	26	27
-3	8	42	42
-3	9	58	58
-2	-16	41	45
-2	-15	28	35
-2	-12	30	37
-2	-11	35	35
-2	-10	44	42
-2	-8	58	54
-2	-6	23	17
-2	-5	20	11
-2	-4	80	75
-2	-3	52	54
-2	-2	48	58
-2	-1	72	86
-2	0	27	26
-2	2	96	86
-2	3	30	27
-2	5	34	27
-2	8	84	80
-2	11	43	43
-1	-15	30	22
-1	-14	42	49
-1	-11	31	27
-1	-10	87	84
-1	-9	74	65
-1	-8	25	22
-1	-7	35	29
-1	-5	44	38
-1	-4	21	17
-1	-3	64	61
-1	-1	59	51
-1	0	60	54
-1	2	24	20
-1	3	66	65
-1	5	38	36
-1	6	38	34
-1	7	94	88
-1	10	32	39
0	-14	38	43
0	-12	39	40
0	-10	74	73
0	-8	90	86
0	-4	65	62
0	-2	91	111
0	0	167	165
0	2	32	27
0	8	29	32

K	L	FO	FC
0	10	55	54
0	12	38	36
	H= 7		
-11	1	33	30
-10	-8	33	30
-10	-7	25	25
-10	-6	26	29
-10	-3	32	30
-10	-1	26	29
-9	-7	27	19
-9	-3	31	32
-9	1	29	32
-8	-11	28	32
-8	-9	29	27
-8	-7	45	41
-8	-6	20	30
-8	-2	29	31
-8	0	24	25
-8	2	29	23
-8	3	26	26
-8	5	24	17
-8	7	26	24
-7	-10	26	20
-7	-9	25	19
-7	-6	43	40
-7	-5	51	53
-7	8	40	36
-6	-12	26	20
-6	-10	31	32
-6	-4	34	37
-6	-2	21	28
-6	-1	40	50
-6	4	53	54
-6	9	37	33
-5	-12	20	26
-5	-11	30	26
-5	-9	50	47
-5	-5	40	35
-5	-2	28	32
-5	-1	33	40
-5	1	26	35
-5	3	34	35
-5	7	49	48
-5	9	32	29
-4	-13	35	32
-4	-10	29	29
-4	-9	70	68
-4	-6	42	40
-4	-5	40	41
-4	-3	21	29
-4	-1	49	63
-4	1	76	86
-4	2	23	14
-3	-12	40	39

K	L	FO	FC
-3	-11	49	46
-3	-10	47	43
-3	-9	23	6
-3	-8	33	31
-3	-6	22	19
-3	-5	65	66
-3	-4	27	26
-3	-3	37	40
-3	-2	28	30
-3	0	26	31
-3	2	33	31
-3	5	44	38
-3	6	30	32
-3	7	49	47
-2	-11	23	22
-2	-10	35	36
-2	-9	44	46
-2	-6	24	27
-2	-5	38	32
-2	-4	83	79
-2	-3	20	21
-2	-2	41	51
-2	0	27	28
-2	2	83	74
-2	3	35	31
-2	5	61	53
-2	6	46	44
-2	10	35	35
-2	11	25	24
-1	-12	30	27
-1	-11	45	42
-1	-10	30	30
-1	-8	73	70
-1	-4	48	42
-1	-3	41	38
-1	-1	53	47
-1	0	22	21
-1	1	66	57
-1	2	27	27
-1	6	23	18
-1	7	24	26
0	-12	34	43
0	-8	52	46
0	-6	112	107
0	-4	70	67
0	2	64	52
0	4	46	37
0	6	112	104
	H= 8		
-9	-1	27	31
-8	-1	41	41
-8	0	24	24
-7	0	25	28
-6	-7	32	31

K	L	FO	FC
-6	-2	28	34
-5	-7	25	20
-5	-5	22	13
-5	-3	21	15
-5	1	33	34
-5	3	33	32
-5	4	23	12
-5	5	46	39
-4	-7	41	41
-4	-6	50	48
-4	-3	22	32
-4	1	33	31
-4	6	49	48
-3	-9	41	38
-3	-7	29	32
-3	-6	65	58
-3	-5	26	20
-3	-4	31	35
-3	-3	24	26
-3	-1	22	21
-3	1	23	20
-3	4	28	26
-3	5	32	31
-2	-10	30	33
-2	-7	24	19
-2	-4	36	35
-2	-3	22	29
-2	-2	27	32
-2	2	43	38
-2	3	29	26
-2	4	74	71
-1	-10	28	27
-1	-5	43	34
-1	-4	40	36
-1	-3	31	26
-1	-1	30	24
-1	2	34	30
-1	5	40	36
-1	7	28	24
0	-12	42	37
0	-10	33	28
0	-8	31	31
0	-6	62	64
0	-4	35	39
0	0	71	62
0	2	25	15
0	4	42	41
	H= 9		
-5	-1	26	25
-5	0	26	18
-5	1	27	25
-4	0	30	24
-3	-3	33	39
-3	-1	31	31

K	L	FO	FC
-3	2	37	32
-3	3	26	25
-2	-7	25	16
-2	-2	35	35
-2	3	29	28
-2	4	31	33
-1	-7	50	42
-1	-4	35	29
-1	3	42	39
0	-8	33	30
0	-4	41	46
0	-2	31	31
0	2	36	33

Structure Factor Table For

1,3-Dimethylimidazolium-2-Thiocyano Bromide

K	L	FO	FC
	H= -8		
0	4	112	115
0	6	86	86
0	8	120	117
0	10	83	90
0	12	43	42
0	14	38	49
1	9	27	24
1	10	40	40
1	12	25	23
1	13	26	28
2	5	51	46
2	7	82	82
2	9	64	67
2	11	86	84
2	12	28	31
2	13	94	103
3	9	25	21
3	13	40	33
4	7	25	27
4	8	70	70
4	10	84	77
4	11	31	28
	H= -7		
0	6	40	46
0	8	25	20
0	10	28	30
0	12	73	75
0	14	89	92
1	0	72	74
1	2	52	51
1	3	65	63
1	4	43	38
1	5	82	80
1	6	52	55
1	7	56	52
1	8	101	96
1	9	73	69
1	10	101	106
1	11	62	59
1	12	94	92
1	13	37	34
1	15	43	40
1	16	28	28
2	1	36	34
2	3	40	40
2	5	26	23
2	7	27	23
2	9	33	30
2	11	33	32
2	12	24	7
2	13	24	17
2	14	25	25
3	0	30	33
3	1	35	33
3	2	59	58
3	3	113	118
3	4	51	49
3	5	113	114
3	6	59	53
3	7	65	69
3	8	94	93
3	9	54	53
3	10	38	30
3	11	55	58
3	12	62	57
3	13	70	74
3	14	45	51
3	15	91	90
4	1	28	25
4	3	40	38
4	5	23	29
4	7	44	46
4	8	25	21
4	12	41	42
4	14	52	49
5	2	53	53
5	3	39	39
5	4	69	70
5	5	46	51
5	6	43	45
5	7	41	43
5	8	72	77
5	9	70	73
5	10	69	71
5	11	85	91
5	12	93	96
5	13	39	38
6	5	27	30
6	8	28	28
	H= -6		
0	0	153	153
0	2	140	143
0	4	207	210
0	6	110	110
0	8	87	97
0	10	123	126
0	12	213	215
0	14	106	111
0	16	75	84
1	0	30	29
1	1	28	32
1	2	44	46
1	4	42	49
1	6	72	63
1	8	21	14
1	9	54	53
1	13	93	89
1	14	52	55
1	16	71	74
2	0	23	19
2	1	78	76
2	2	22	22
2	3	110	109
2	5	128	124
2	7	191	183
2	8	43	47
2	9	152	150
2	11	113	113
2	13	94	95
2	15	48	49
2	17	71	75
3	3	39	39
3	5	69	76
3	9	65	65
3	10	31	29
3	11	56	54
3	12	50	50
3	13	53	51
3	15	25	29
4	0	69	66
4	1	37	39
4	2	79	75
4	3	49	49
4	4	128	133
4	5	29	30
4	6	104	103
4	7	56	53
4	8	97	100
4	9	28	24
4	10	100	99
4	12	85	82
4	13	31	26
4	14	78	81
4	16	55	53
5	2	23	26
5	5	23	25
5	6	33	35
5	8	26	24
5	14	43	42
5	15	42	47
6	1	71	70
6	2	43	45
6	3	81	77
6	4	50	53
6	5	93	95
6	7	103	99
6	9	55	53
6	11	76	79
6	12	35	41
6	13	87	87
6	14	33	38
7	4	29	30
7	6	26	26
7	9	25	29
7	10	53	55
7	12	31	30
8	5	32	29
8	6	70	73
8	8	112	112
	H= -5		
0	2	75	80
0	4	78	81
0	6	29	33
0	8	175	161
0	10	87	88
0	12	30	29
0	14	51	51
0	16	48	50
0	18	72	75
1	0	59	60
1	1	103	104
1	2	81	82
1	3	102	94
1	4	158	152
1	5	115	104
1	6	210	204
1	7	102	91
1	8	152	143
1	9	105	98
1	10	21	20
1	11	73	67
1	12	86	89
1	13	102	99
1	14	68	63
1	15	49	53
1	16	79	84
1	18	45	54
2	4	32	28
2	5	62	53
2	10	27	30
2	11	60	57
2	13	82	84
2	14	23	30
2	15	75	77
2	17	61	64
3	0	78	77
3	1	161	161
3	2	76	74
3	3	109	115
3	4	124	130
3	5	65	66
3	6	85	77
3	7	93	93
3	8	98	95
3	9	170	176
3	10	86	84

K	L	FO	FC
3	11	149	154
3	12	91	86
3	13	100	102
3	14	54	57
3	15	49	49
3	16	43	44
4	1	35	35
4	3	74	79
4	7	58	56
4	8	77	84
4	10	37	37
4	12	35	37
4	13	55	56
4	14	72	76
4	15	41	38
4	16	32	31
5	0	110	112
5	1	65	68
5	2	59	54
5	3	83	85
5	4	113	121
5	5	117	120
5	6	131	142
5	7	125	130
5	8	138	139
5	9	74	75
5	10	43	51
5	11	42	45
5	12	85	84
5	13	47	53
5	14	57	64
5	15	57	60
5	16	54	53
6	2	31	39
6	3	34	36
6	4	50	52
6	5	28	31
6	8	50	53
6	9	57	61
6	11	39	48
6	13	34	32
6	14	24	18
6	15	25	29
7	0	100	99
7	1	65	63
7	2	77	76
7	3	84	84
7	4	48	46
7	5	72	73
7	7	74	79
7	8	83	85
7	9	77	72
7	10	85	87
7	11	54	54
7	12	95	103
7	13	54	51

K	L	FO	FC
8	4	26	25
8	3	40	43
8	4	37	35
8	5	67	66
8	6	65	61
8	7	34	35
8	8	40	44

H= -4

K	L	FO	FC
0	0	270	277
0	2	160	164
0	4	159	156
0	6	166	167
0	8	443	438
0	10	197	197
0	12	164	169
0	14	66	72
0	16	77	84
0	18	49	57
1	0	41	38
1	2	62	65
1	3	17	15
1	4	39	39
1	5	50	51
1	6	44	36
1	7	28	19
1	8	24	21
1	9	141	129
1	10	121	118
1	12	104	106
1	13	47	46
1	14	34	34
1	16	27	30
1	17	58	57
2	0	33	33
2	1	173	179
2	3	258	261
2	4	73	76
2	5	254	255
2	7	202	198
2	9	122	122
2	10	30	15
2	11	134	137
2	13	148	149
2	15	92	96
2	16	27	34
2	17	77	90
3	1	105	109
3	2	22	13
3	5	81	81
3	6	35	31
3	7	95	94
3	8	30	35
3	9	43	42
3	10	47	47

K	L	FO	FC
3	11	28	28
3	12	35	30
3	13	23	26
3	14	37	39
3	15	73	76
3	17	68	71
4	0	172	173
4	1	50	48
4	2	165	163
4	3	78	75
4	4	153	159
4	5	50	44
4	6	134	133
4	7	37	44
4	8	166	164
4	9	45	49
4	10	145	149
4	12	77	74
4	13	40	37
4	14	95	93
4	15	46	48
4	16	57	58
5	0	30	38
5	4	43	41
5	6	30	41
5	7	25	25
5	9	40	35
5	10	87	89
5	11	53	56
5	12	40	41
5	13	52	54
5	14	43	51
5	16	39	41
6	0	52	57
6	1	112	115
6	2	22	19
6	3	136	135
6	4	22	18
6	5	100	101
6	6	21	21
6	7	143	142
6	8	83	83
6	9	121	121
6	10	46	53
6	11	97	94
6	13	89	93
6	15	28	27
7	0	47	48
7	1	33	27
7	2	43	46
7	3	29	32
7	4	21	17
7	6	91	97
7	7	24	24
7	9	33	30
7	11	29	30

K	L	FO	FC
7	13	49	51
7	14	31	27
8	0	102	97
8	1	37	32
8	2	119	118
8	3	35	32
8	4	165	165
8	5	23	21
8	6	94	91
8	7	40	42
8	8	76	81
8	9	25	17
8	10	52	53
8	12	87	86
9	0	40	36
9	4	26	25
9	8	26	28
9	9	27	29
9	10	45	40
10	5	55	61

H= -3

K	L	FO	FC
0	0	117	114
0	4	248	223
0	6	104	102
0	8	85	69
0	12	106	113
0	14	127	127
0	16	60	65
1	0	230	209
1	1	153	157
1	2	288	274
1	3	170	160
1	4	248	229
1	5	142	131
1	6	38	27
1	7	108	98
1	8	139	136
1	9	201	188
1	10	142	131
1	11	74	68
1	12	172	166
1	13	45	43
1	14	71	73
1	15	48	46
1	16	32	23
1	17	41	41
2	0	31	27
2	1	34	28
2	2	38	42
2	3	55	58
2	5	19	16
2	6	44	44
2	7	30	27
2	9	141	138

K	L	FO	FC
2	10	45	52
2	11	110	110
2	13	52	54
2	15	39	43
2	17	45	48
3	0	160	160
3	1	107	112
3	2	119	115
3	3	155	158
3	4	137	136
3	5	257	265
3	6	163	158
3	7	258	263
3	8	130	121
3	9	178	178
3	10	89	87
3	11	50	53
3	12	107	102
3	13	32	36
3	14	31	30
3	15	80	96
3	16	43	39
3	17	74	76
4	1	44	40
4	2	73	69
4	3	86	80
4	4	71	77
4	5	24	26
4	6	38	42
4	7	23	16
4	8	46	42
4	9	106	103
4	10	68	73
4	11	54	49
4	12	61	55
4	13	34	31
4	14	63	67
4	15	36	36
4	16	35	40
5	0	154	159
5	1	163	160
5	2	167	169
5	3	176	186
5	4	202	211
5	5	99	104
5	6	79	90
5	7	57	60
5	8	120	118
5	9	110	120
5	10	113	120
5	11	89	92
5	12	104	111
5	13	84	92
5	14	45	49
5	15	54	57
5	16	57	62
6	0	38	40
6	2	29	23
6	4	61	61
6	5	69	66
6	6	38	34
6	8	44	42
6	9	52	50
6	10	34	32
6	11	39	39
6	13	45	51
6	14	45	46
6	15	39	39
7	0	51	47
7	1	113	109
7	3	117	116
7	4	120	127
7	5	87	84
7	6	136	142
7	7	92	95
7	8	141	147
7	9	99	96
7	11	53	47
7	12	33	34
7	13	64	63
8	0	25	22
8	1	25	29
8	2	27	26
8	3	25	23
8	4	41	42
8	8	66	66
8	10	64	66
8	11	36	40
8	12	38	38
9	0	42	40
9	1	85	83
9	2	71	67
9	3	50	47
9	4	85	83
9	5	54	54
9	6	75	71
9	8	76	74
9	9	36	30
9	10	75	68
10	3	48	43
10	5	56	57

H= -2

K	L	FO	FC
0	0	292	299
0	2	249	236
0	6	281	272
0	8	193	197
0	10	106	107
0	12	141	137
0	14	121	131
0	16	98	103
1	0	151	142
1	1	29	29
1	2	48	54
1	3	130	115
1	4	44	37
1	5	226	196
1	6	156	146
1	7	16	12
1	8	145	144
1	9	51	47
1	10	54	44
1	11	29	27
1	13	99	96
1	14	39	39
1	15	26	24
1	16	44	45
1	17	40	36
2	0	107	93
2	1	284	286
2	2	18	4
2	3	300	312
2	4	22	20
2	5	207	207
2	6	27	17
2	7	231	225
2	8	28	21
2	9	226	224
2	10	26	25
2	11	183	184
2	12	41	46
2	13	113	115
2	15	27	27
3	1	84	88
3	2	29	33
3	3	64	64
3	4	16	11
3	5	41	35
3	6	49	53
3	7	57	54
3	8	24	17
3	10	69	70
3	11	113	119
3	12	24	21
3	13	111	115
3	14	53	53
3	15	42	46
3	16	41	46
4	0	236	238
4	1	18	16
4	2	186	168
4	3	75	72
4	4	219	216
4	5	57	58
4	6	198	206
4	7	22	30
4	8	148	148
4	9	76	72
4	10	139	136
4	11	74	74
4	12	91	94
4	13	25	32
4	14	64	58
4	15	45	44
4	16	41	46
5	1	67	70
5	2	46	51
5	3	28	29
5	5	40	39
5	6	86	90
5	7	72	78
5	8	42	44
5	9	58	58
5	10	67	69
5	11	22	17
5	12	30	36
5	13	27	26
5	14	42	42
6	0	24	14
6	1	114	112
6	2	61	63
6	3	207	208
6	4	94	94
6	5	183	182
6	6	68	74
6	7	124	122
6	9	130	131
6	10	46	47
6	11	76	73
6	12	26	24
6	13	68	66
6	14	27	28
7	0	39	29
7	2	107	108
7	5	43	40
7	6	39	42
7	7	31	34
7	8	38	33
7	9	43	47
7	10	50	49
7	11	26	25
7	12	58	59
7	13	58	58
8	0	211	210
8	2	110	109
8	3	47	53
8	4	90	99
8	5	45	45
8	6	83	82
8	8	149	149
8	9	31	36
8	10	107	107
8	11	41	39

K	L	FO	FC
8	12	82	82
9	3	25	29
9	5	28	33
9	9	49	49
10	1	73	73
10	2	31	25
10	3	146	137
10	5	141	140
10	7	76	79
11	3	35	35

H= -1

K	L	FO	FC
0	0	267	303
0	1	12	0
0	2	47	41
0	4	144	136
0	6	20	16
0	8	159	152
0	10	159	156
0	12	93	95
0	14	80	82
1	0	203	196
1	1	189	191
1	2	20	24
1	3	67	73
1	4	273	252
1	5	283	277
1	6	221	206
1	7	110	108
1	8	243	232
1	9	88	79
1	10	119	118
1	11	65	65
1	12	42	39
1	13	84	80
1	14	23	27
1	16	28	36
2	1	83	92
2	2	19	14
2	5	133	139
2	6	65	63
2	7	107	106
2	8	18	18
2	9	71	70
2	10	20	11
2	11	36	39
2	12	24	17
2	13	58	57
2	15	90	88
3	0	96	107
3	1	412	420
3	2	261	254
3	3	312	326
3	4	149	158
3	5	235	236
3	6	117	113
3	7	92	94
3	8	150	154
3	9	85	85
3	10	56	53
3	11	122	126
3	12	72	70
3	13	135	136
3	14	43	46
3	15	44	46
4	0	68	63
4	2	32	31
4	4	37	35
4	5	120	119
4	6	89	92
4	7	62	59
4	8	54	49
4	9	52	51
4	10	61	64
4	11	56	59
4	12	60	63
4	14	63	63
4	15	34	35
5	0	193	193
5	1	115	120
5	2	110	116
5	3	66	69
5	4	210	209
5	5	183	194
5	6	153	156
5	7	125	128
5	8	140	151
5	9	128	134
5	10	87	83
5	11	65	71
5	12	84	91
5	13	28	32
6	0	89	83
6	1	95	75
6	3	21	11
6	4	67	67
6	5	40	35
6	6	30	22
6	7	30	31
6	8	22	15
6	9	77	77
6	10	62	66
6	11	39	35
6	12	31	29
6	13	66	69
7	0	153	152
7	1	140	129
7	2	191	190
7	3	102	97
7	4	167	171
7	5	125	124
7	7	96	91
7	8	44	47
7	9	88	84
7	10	43	47
7	11	44	41
7	12	83	87
7	13	51	48
8	0	57	59
8	4	81	83
8	6	69	71
8	7	40	45
9	0	89	87
9	1	46	49
9	2	93	87
9	3	32	30
9	4	113	109
9	5	52	49
9	6	81	75
9	7	74	72
9	8	30	27
9	9	71	65
9	10	47	43
10	1	54	57
10	3	26	29
10	5	25	26
10	6	30	23
10	7	29	23
11	0	32	30
11	1	46	47
11	2	41	35
11	3	29	28
11	4	33	31

H= 0

K	L	FO	FC
0	2	239	218
0	3	14	0
0	4	267	238
0	6	206	187
0	8	233	215
0	10	176	177
0	12	158	160
0	14	54	57
1	1	130	124
1	2	206	227
1	3	35	29
1	4	124	111
1	5	59	66
1	6	24	16
1	9	110	107
1	10	51	54
1	11	24	21
1	12	51	48
1	13	48	48
1	14	81	80
2	0	18	18
2	1	236	239
2	3	391	409
2	4	84	76
2	5	286	273
2	7	230	234
2	8	49	55
2	9	170	168
2	10	30	24
2	11	55	55
2	13	70	74
2	15	55	56
3	1	99	94
3	2	73	68
3	3	79	90
3	4	44	31
3	6	87	87
3	7	135	138
3	9	128	126
3	10	62	59
3	11	53	56
3	12	40	47
4	0	340	335
4	1	104	90
4	2	183	184
4	4	181	184
4	5	112	104
4	6	201	201
4	7	68	74
4	8	141	141
4	9	31	40
4	10	81	75
4	11	60	60
4	12	72	74
4	14	60	61
5	2	132	132
5	3	81	94
5	5	43	45
5	6	50	51
5	8	45	55
5	10	43	44
5	12	24	34
5	13	45	47
6	0	128	123
6	1	194	196
6	2	71	77
6	3	169	172
6	4	24	17
6	5	149	151
6	6	38	40
6	7	106	102
6	8	41	45
6	9	104	104
6	10	23	34
6	11	69	64
6	12	32	35
7	2	69	73

K	L	FO	FC
7	4	53	48
7	5	70	69
7	6	64	69
7	8	63	65
7	9	55	57
7	10	55	54
7	11	35	32
8	0	132	136
8	1	44	46
8	2	94	90
8	3	21	6
8	4	187	187
8	5	46	48
8	6	139	146
8	7	37	33
8	8	105	102
8	10	41	43
9	1	23	30
9	2	23	24
9	3	25	23
9	5	38	36
9	8	63	59
10	0	24	19
10	1	152	146
10	3	91	96
10	5	39	37
10	6	29	28
10	7	54	58
11	1	24	30
11	3	40	43

H= 1

K	L	FO	FC
0	0	264	303
0	2	115	100
0	4	288	250
0	6	153	145
0	8	80	76
0	10	94	92
0	14	60	60
1	0	262	196
1	1	240	274
1	2	353	352
1	3	77	89
1	4	270	266
1	5	146	141
1	6	113	114
1	7	89	90
1	8	68	65
1	9	109	98
1	10	47	48
1	11	27	31
1	12	53	56
1	13	47	47
1	14	46	44
2	0	13	7

K	L	FO	FC
2	1	233	241
2	2	88	76
2	4	35	33
2	5	39	36
2	7	50	51
2	9	71	65
2	11	89	91
2	13	65	65
3	0	93	107
3	1	246	239
3	2	171	174
3	3	50	59
3	4	181	182
3	5	133	130
3	6	57	62
3	7	174	175
3	8	100	100
3	9	165	167
3	10	66	67
3	11	61	62
3	12	43	41
4	0	66	63
4	1	138	133
4	2	59	54
4	3	58	59
4	4	79	81
4	5	99	93
4	6	31	32
4	7	58	59
4	8	51	51
4	9	38	39
4	10	78	73
4	11	36	38
4	12	42	41
4	13	26	18
5	0	200	193
5	1	204	220
5	2	218	221
5	3	137	139
5	4	173	184
5	5	157	165
5	6	74	71
5	7	75	77
5	8	123	128
5	9	46	45
5	10	48	46
5	11	40	41
5	12	34	36
6	0	88	83
6	1	75	69
6	2	39	35
6	4	37	42
6	5	65	70
6	6	73	77
6	7	39	35
6	9	61	65

K	L	FO	FC
6	11	31	34
7	0	154	152
7	1	143	139
7	2	25	23
7	3	86	83
7	4	46	49
7	5	114	115
7	6	68	69
7	7	70	66
7	8	110	115
7	9	51	49
7	10	64	61
8	0	60	59
8	2	35	39
8	3	33	39
8	4	22	22
8	9	25	25
9	0	88	87
9	1	57	54
9	2	94	94
9	3	86	84
9	4	44	41
9	5	77	74
9	6	47	45
10	1	26	25
10	3	24	17
10	5	47	45
11	0	31	30
11	1	76	70

H= 2

K	L	FO	FC
0	0	289	299
0	2	140	115
0	4	320	301
0	6	240	226
0	8	180	178
0	10	69	67
0	12	36	36
1	0	146	142
1	1	31	17
1	2	19	21
1	3	25	31
1	4	82	73
1	5	93	96
1	6	83	84
1	8	56	52
1	9	55	57
1	10	78	76
1	11	26	27
1	12	28	35
2	0	104	93
2	1	325	330
2	3	261	282
2	4	50	54
2	5	143	144

K	L	FO	FC
2	6	37	36
2	7	90	86
2	9	110	113
2	11	73	71
3	1	60	63
3	2	66	66
3	3	165	177
3	4	23	20
3	5	125	123
3	6	63	65
3	8	38	41
3	11	35	39
3	12	26	24
4	0	234	238
4	1	114	108
4	2	145	150
4	3	67	77
4	4	186	189
4	5	56	58
4	6	107	107
4	7	67	70
4	8	75	75
4	10	80	80
5	2	34	25
5	6	55	57
5	8	40	42
5	9	51	53
5	10	47	49
5	11	46	45
6	0	30	14
6	1	167	170
6	2	43	44
6	3	139	143
6	4	55	57
6	5	96	96
6	6	55	56
6	7	89	88
6	8	34	29
6	9	81	79
7	0	37	29
7	1	23	28
7	2	62	56
7	4	50	55
7	5	55	57
7	6	53	53
7	9	25	33
8	0	202	210
8	1	47	50
8	2	121	126
8	3	46	44
8	4	115	116
8	6	55	54
9	1	25	13
9	4	35	37
9	6	33	30
10	1	46	45

K	L	FO	FC
10	2	27	22
10	3	72	73

H= 3

K	L	FO	FC
0	0	115	114
0	2	141	133
0	4	76	75
0	6	49	44
0	10	74	71
1	0	201	209
1	1	100	105
1	2	148	149
1	3	91	97
1	4	46	49
1	5	131	127
1	6	55	55
1	7	21	23
1	8	89	90
1	9	55	53
1	10	49	49
2	0	29	27
2	1	56	54
2	3	27	21
2	5	77	75
2	7	97	98
2	9	49	47
3	0	159	160
3	1	109	111
3	2	94	102
3	3	171	176
3	4	86	85
3	5	201	204
3	6	75	76
3	7	54	54
3	8	55	53
4	1	89	93
4	2	18	16
4	3	56	59
4	4	53	55
4	5	44	46
4	6	44	40
4	7	43	45
4	8	38	39
5	0	157	159
5	1	118	126
5	2	93	96
5	3	69	74
5	4	111	117
5	5	66	63
5	6	50	53
5	7	43	44
5	8	62	61
5	9	59	60
6	0	40	40
6	1	73	78
6	2	60	66
6	5	54	59
6	7	34	36
7	0	44	47
7	1	91	92
7	2	88	88
7	3	64	66
7	4	110	114
7	5	72	70
7	6	66	63
7	7	38	39
8	0	24	22
8	6	46	50
9	0	41	40
9	1	66	62
9	2	71	69
9	4	65	61
10	1	43	44

H= 4

K	L	FO	FC
0	0	264	277
0	2	176	171
0	4	212	210
0	6	63	60
0	8	35	34
1	0	35	38
1	1	44	47
1	2	53	55
1	4	36	33
1	5	32	35
1	6	81	79
1	8	26	22
1	9	34	29
2	0	32	33
2	1	157	170
2	2	28	29
2	3	89	87
2	4	21	18
2	5	101	104
2	7	98	99
3	1	73	72
3	2	28	26
3	4	24	23
3	7	29	30
4	0	169	173
4	1	50	51
4	2	78	78
4	3	56	60
4	4	95	98
4	6	77	82
4	7	26	26
5	0	30	38
5	2	28	29
5	3	34	32
5	5	34	35
5	6	59	55
5	7	35	37
6	0	56	57
6	1	115	114
6	2	43	49
6	3	81	85
6	4	30	26
6	5	69	66
7	0	44	48
7	1	28	33
7	2	32	29
7	3	24	21
7	4	25	26
8	0	98	97
8	2	42	40
9	0	41	36

H= 5

K	L	FO	FC
0	2	42	42
0	6	50	46
1	0	54	60
1	1	82	85
1	2	68	67
1	3	28	30
1	4	77	76
1	5	57	58
1	6	56	55
2	1	55	59
2	3	46	50
2	5	46	47
3	0	75	77
3	1	144	153
3	2	75	79
3	3	50	55
3	4	38	37
3	5	31	30
3	6	33	37
4	1	43	45
4	2	43	41
4	3	37	33
4	4	25	25
5	0	109	112
5	1	49	49
5	2	61	65
5	3	53	51
5	4	51	48
6	1	28	34
7	0	97	99
7	1	47	48
7	2	56	53

H= 6

K	L	FO	FC
0	0	145	153
0	2	47	46
0	4	51	50
1	0	29	29
1	1	26	27
1	2	41	38
2	1	103	109
2	3	76	78
3	3	35	31
4	0	66	66
4	1	27	27
4	2	68	72

H= 7

K	L	FO	FC
1	0	69	74
1	1	41	42
3	0	31	33

REFERENCES

1. W. A. Sheppard and J. Diekmann, J. Amer. Chem. Soc., 86, 1891 (1964).

2. B. Zwanenburg, L. Thijs, and J. Strating, Rec. Trav. Chim. Pays-Bas, 86, 577 (1967).

3. B. Zwanenburg, L. Thijs, and J. Strating, Tetrahedron Letts., 4461 (1969).

4. B. Zwanenburg, L. Thijs, and Strating, ibid., 65 (1966).

5. E. U. Elam, F. H. Rash, J. T. Dougherty, V. W. Goodlett, and K. C. Brannock, J. Org. Chem., 37, 3818 (1972).

6. W. G. Phillips and K. W. Ratts, J. Org. Chem., 37, 3818 (1972).

7. E. M. Burgess and H. R. Penton, Jr., J. Amer. Chem. Soc., 95, 279 (1973).

8. H. R. Penton, Jr., "The Chemistry of Thione S-Imides," Thesis, Georgia Institute of Technology, 1973.

9. H. Nozaki, Tetrahedron Letts., 3651 (1969).

10. W. J. Middleton, J. Org. Chem., 31, 3731 (1966).

11. S. Tamagaki and S. Oae, Tetrahedron Letts., 1159 (1972).

12. R. M. Kellogg, S. Wassenaar, and J. Butler, J. Org. Chem., 37, 3045 (1972).

13. R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie Academic Press (1971).

14. J. P. Snyder, J. Amer. Chem. Soc., 96, 5005 (1974).

15. J. P. Snyder and B. Schilling, ibid., 97, 4422 (1975).

16. J. C. Martin, Abstracts of the 23rd National Organic Symposium, Tallahassee, Florida, pp. 127-137, 1973.

17. E. F. Perozzi, J. C. Martin, and I. C. Paul, J. Amer. Chem. Soc., 96, 6735 (1974).

18. J. I. Musher, Angew. Chem., Int. Ed. Engl., 8, 54 (1969).

19. A. Rauk, L. C. Allen, and K. Mislow, J. Amer. Chem. Soc., 94, 3035 (1972).

20. J. B. Florey and L. C. Cusachs, ibid., 94, 3040 (1972).

21. R. Hoffmann, J. M. Howell, and E. L. Mutterties, ibid., 94, 3047 (1972).

22. J. I. Musher, ibid., 94, 1370 (1972).

23. R. Hoffmann and M. M. L. Chen, ibid., 98, 1647 (1976).

24. R. Grigg, T. J. King, and G. Shelton, Chem. Comm., 56 (1970).

25. J. Amer. Chem. Soc., 74, 1816 (1952).

26. V. V. Kozlov, Zhur. Obshchei Khim., 18, 757-66 (1948).

27. Mme. Ramart-Lucas and J. Hock, Ann. Chim., [10], 13, 385-422 (1930).

28. W. J. Middleton, E. L. Buhle, J. G. McNally, Jr., and M. Zanger, J. Org. Chem., 30, 2384 (1965).

29. K. Gleu and R. Schaarschmidt, Ber., 72, 1249 (1939).

30. B. B. Corson and W. L. Benson, Org. Syn., Col. Vol. 2, 273-275.

31. D. G. I. Felton, J. Chem. Soc., 515-516 (1955).

32. Ken-ichi Kudo, Bull. Chem. Soc., 35, 1490 (1962).

33. M. J. S. Dewar. R. C. Bingham, and D. H. Lo, J. Amer. Chem. Soc., 97, 1285 (1975).

34. C. J. Ireland and J. S. Pitey, J. Chem. Soc., Chem. Commun., 4 (1972); K. Kudo, Bull. Chem. Soc. Japan, 35, 1490 (1962); D. G. I. Felton and S. F. D. Orr, J. Chem. Soc., 2170 (1955).

35. A. T. Christensen and E. Thom, Acta. Cryst., B27, 581 (1971).

36. R. H. Levin and J. D. Roberts, Tetrahedron Letts., 135 (1973).

37. H. O. Kalinowski and H. Kessler, Angew. Chem., Int. Ed. Engl., 13, 90 (1974).

38. M. Karplus and J. A. Pople, J. Chem. Phys., 38, 2803 (1963); M. Karplus and T. P. Das, ibid., 34, 1683 (1961).

39. J. A. Pople, D. L. Beveridge, and P. A. Dobosh, ibid., 47, 2026 (1967).

40. R. S. Mulliken, ibid., 23, 1833 (1955).

41. For example, see J. I. Musher, J. Amer. Chem. Soc., 94, 1370 (1972); A. Streitwieser and J. E. Williams, Jr., ibid., 97, 191

42. E. J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 84, 3782 (1962); 87, 1353 (1965); A. W. Johnson, V. J. Hruby, and J. L. Williams, ibid., 86, 918 (1964); V. Franzen and H. E. Driessen, Chem. Ber., 96, 1881 (1963); C. G. Swain and E. R. Thorton, J. Amer. Chem. Soc., 83, 4033 (1961).

43. H. Nozaki, D. Tunemoto, Z. Morita, K. Nakamura, K. Watanobe, M. Takaku, and K. Kondo, Tetrahedron, 23, 4279 (1967).

44. S. Tamagaki and I. Hatanaka, Chem. Lett., 301-302 (1976).

45. E. L. Mutterties and R. A. Schunn, Quart. Rev. Chem. Soc., 20, 245 (1966); R. E. Rundle, Surv. Prog. Chem., 1, 81 (1963).

46. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, "The Purification of Laboratory Chemicals," Pergamon Press Ltd. (1966).

47. Programs utilized were Zalkin's FORDAP Fourier summation program, Iber's NUCLS modification of the Busing-MartinpLevy least-squares program, Doeden's RBANG rigid group orientation program, Stewart's ABSORB absorption correction program from the X-Ray 72 system, and Johnson's ORTEP program.

VITA

Anthony J. Arduengo, III, son of Mr. and Mrs. Anthony J. Arduengo, Jr., was born in Tampa, Florida on July 9, 1952.

He was graduated from Walker High School, Atlanta, Georgia in June, 1970, and received his Bachelor of Science degree in Chemistry from the Georgia Institute of Technology, Atlanta, Georgia in June of 1974. He immediately began graduate work in the School of Chemistry at the Georgia Institute of Technology.